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HETEROTRIACIDS

V. HETEROTRIACIDS OF PHOSPHORUS AND SILICON WITH VARYING COMPOSITION OF ADDENDS, CONTAINING MOLYBDENUM AND TUNGSTEN

A. I. Kokorin and N. A. Polotebnova

The literature does not contain any information about the preparation in the free state of heterotriacids containing molybdenum and tungsten in various ratios. There are some data [1] to the effect that a mixture of derivatives of phosphomolybdic acids of the series: $3H_2O \cdot P_2O_5 \cdot 18(WO_3 + MoO_3)$ and $3H_2O \cdot P_2O_5 \cdot 24(WO_3 + MoO_3)$ is obtained. It is suggested that at high temperature members of the 18-series change in the 24-series; their stability depends on the MoO_3 content and on the temperature. The soluble ammonium salt of the 18-series with a high content of MoO_3 easily changes into the insoluble salt of the 24-series. In an investigation of the reducing power of these derivatives, Wu [2] arrived at the conclusion that this power is proportional to the molybdenum content.

In 1924 and 1927 the I. G. Farbenindustrie issued patents on the preparation of sodium and ammonium salts of phosphomolybdotungstic acids in which the total content of molybdenum and tungsten was $18(WO_3 + MoO_3)$ and $24(WO_3 + MoO_3)$. The salts were prepared according to the following recipe: 100 parts sodium tungstate and 25 parts molybdate were dissolved in 225 parts water; addition was made of 85 parts 85% phosphoric acid, 115 parts hydrochloric acid (19° Baumé) and 2 parts nitric acid. The mixture was slowly boiled; after cooling, large crystals of the sodium salt of the 24-acid came down. The ammonium salt of the 18-acid was obtained from the filtrate by precipitation [1].

In 1927 and 1928 patents were taken out for the preparation of products of reduction of these salts as intermediates for lake colors [1].

A solution for colorimetric determinations of thallium and antimony is prepared by boiling phosphomolybdic acid with phosphoric acid and sodium tungstate; the element ratio is P: Mo: W = 23.5: 1: 3 [3]. The reagent undoubtedly contains an excess of phosphoric acid, tungstate, and various reaction products including a certain amount of phosphomolybdotungstic acid. Use is also made for penicillin analysis of a reagent containing phosphomolybdotungstic acid in solution [4].

We proposed to synthesize, by the etherate method, heterotriacids with phosphorus and silicon as central atoms and molybdenum and tungsten as addends in a complex anion in various ratios. Another objective was to separate these acids in the crystalline state.

EXPERIMENTAL

Synthesis. In the initial stage of the investigation we tried to apply the etherate method to the separation in the free state of phosphomolybdotungstic acid from the solution used for determination of thallium and antimony [3]. Optimum conditions were established for the isolation in the free state from the solution mentioned of crystalline phosphomolybdotungstic acid whose analysis revealed a ratio of P: Mo: W = 1: 8: 4.* On the basis of the Miolati-Rosenheim theory this product should be assigned the formula $H_7[P(Mo_2O_7)_4(W_2O_7)_2]$.

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* In this stage much assistance was rendered by A. A. Pareli.

For the purpose of preparation of heterotriacids with a given, variable content of molybdenum and tungsten, which should contain a strictly specified amount of molybdenum and tungsten, we aimed above all at syntheses from stoichionmetric ratios of components. A second very important factor, as revealed in our preceding investigations on synthesis of heterotriacids, in particular the synthesis of silicotungstovanadic acid [5], is the character of the tungstate anions. In a series of cases the tungstate ion is most easily inserted into complexes of heterotriacids when it is in the form of metatungstate. Since great preparative difficulties attend the isolation of metatungstate in the free state, while its preparation in solution by boiling tungstate with tungstic acid gives products of reaction of variable composition, in the closing stage of the investigation we started from a solution of sodium metatungstate obtained from normal tungstate according to the reaction:

$$\text{a)}\ 9Na_2WO_4 + 18HCl = \downarrow 9WO_3 + 18NaCl + 9H_2O,$$

$$\text{b)}\ 3Na_2WO_4 + 9WO_3 + 3H_2O = Na_6H_4[H_2(W_2O_7)_6]$$

$$12Na_2WO_4 + 18HCl = Na_6H_4[H_2(W_2O_7)_6] + 18NaCl + 6H_2O.$$

This process proceeds the most elegantly if a weighed amount of $Na_2WO_4 \cdot 2H_2O$ (chem. pure) is dissolved in approximately the fivefold amount of distilled water with heating. Then to the boiling solution is slowly added, dropwise with vigorous stirring, from a buret 6 N hydrochloric acid in amount equivalent to 1.5 moles HCl per mole tungstate. The WO_3 precipitate formed during the titration dissolves on shaking. On addition of the whole of the specified amount of hydrochloric acid, formation of precipitate ceases. It is not uninteresting to mention in passing that this corresponds so closely to the calculated amount that it served as a check on the purity of the tungstate used.

Sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ (chem. pure), dissolved in 3 times the amount of water, was converted into metamolybdate by the same method. It should be mentioned that the solution acquires a yellowish color after all the hydrochloric acid has been run in.

In the synthesis of heterotriacids containing phosphorus, we used $Na_2HPO_4 \cdot 12H_2O$, and for acids containing silicon we used $Na_2SiO_3 \cdot 9H_2O$, dissolved in small quantities of water. In separate experiments we took 3 g phosphate and 4.26 g silicate.

Amounts of starting substances were calculated on the basis of the Mo : W ratios (per part by weight of central atom) of 10 : 2, 8 : 4, 6 : 6, 4 : 8 and 2 : 10.

To a mixture of hot solutions of metatungstate and metamolybdate was added a solution of phosphate or silicate. Introduction of the solution of silicate (approximately 50 ml) must be effected slowly (dropwise) in order to avoid formation of a precipitate of silicic acid. After introduction of small amounts of H_2SO_4 (1 : 1) until the color of the solution is definitely yellow, the mixture of starting substances is boiled. In the synthesis of heterotriacids of phosphorus, boiling is carried out for 2 hours in a flask under a refulx condenser (glass fitting); in the synthesis of silicic triacids the boiling is for 1 hour in an open flask. In the latter case the volume of liquid at the end of boiling is 150 ml.

Etherate was prepared by adding ether and sulfuric acid (1 : 1) dropwise with stirring to the cold solution in a separating funnel. Formation of etherate is an exothermic reaction and the success of the preparation depends upon periodic cooling under the tap with slight shaking. If turbidity develops during addition of the sulfuric acid, its further addition must be stopped until the solution has cleared. The etherate of phosphomolybdotungstic acids begins to form at an acidity up to 1 N concentration of the introduced H_2SO_4, and the etherate of the silicic acids at up to 1.8 N. Further addition of acid increases the amount of etherate. The acid was added in small portions until etherate ceased to be formed. Sometimes the aqueous layer above the etherate was cloudy. On standing for 12 hours, the liquid above the etherate became clear. We propose to take the absence of precipitate in the aqueous phase as the criterion of formation of heterotriacid with the calculated composition.

The settled etherate was run off into a small crystallizer (a wide dish) and a little water was added. Crystallization was effected isothermally on standing. If at any stage of the synthesis the solutions acquired a green or blue color (due to partial reduction of the heterotriacids), the obtained products were at the end dissolved in water, a little (few drops) conc. HNO_3 was added, and a second crystallization was carried out. In this connection, it should be noted that nitric acid must only be added after complete removal of ether.

The yield of crystalline products in our experiments was 70-75% of the theoretical.

Analysis. All the prepared phosphomolybdotungstic and silicomolybdotungstic acids were analyzed for their content of water of crystallization, phosphorus, silicon, molybdenum and tungsten. Water of crystallization was determined by drying in a drying cupboard, phosphorus by precipitation as magnesium ammonium phosphate, silicon by precipitation of silicic acid from alkaline solution with the help of NH_4Cl in presence of potash alum [6]. Here it should be noted that determination of silicon by the generally accepted method – treatment of the calcined residue (oxides) at 400° with hydrofluoric acid in presence of H_2SO_4 – did not give good results. Under these conditions (in presence of large amounts of WO_3) silicon is removed too slowly and far from completely. A check of the method [6] with appropriate quantitative ratios of tungsten and silicon revealed good results. Molybdenum was determined by a volumetric method developed by us specially for its determination in presence of large amounts of tungsten [7] and based upon titration of the test solution with a solution of trivalent titanium sulfate in 4N H_2SO_4 in presence of monoindigo sulfonate as indicator. Tungsten was determined by the usual gravimetric method in the form of WO_3 (Table 1 and 2).

TABLE 1

Analytical results for phosphomolybdotungstic acids

Acid Number	Weight of sample (in mg)	H_2O		P		Mo		W		Ratio P : Mo : W : H_2O
		(mg)	(mg-mole)	(mg)	(mg-mole)	(mg)	(mg-mole)	(mg)	(mg-mole)	
I	845.6	132.0	7.30	8.60	0.280	269.0	2.86	102.1	0.55	1 : 10.21 : 1.96 : 26.44
II	823.2	132.3	7.35	8.30	0.270	211.2	2.25	200.6	1.08	1 : 8.33 : 4.00 : 27.52
III	1025.3	122.8	6.80	10.80	0.350	202.0	2.20	382.2	2.07	1 : 6.28 : 5.91 : 19.48
IV	1135.3	141.0	7.80	11.95	0.385	153.6	1.59	570.4	3.10	1 : 4.12 : 8.04 : 20.25
V	990.1	98.5	5.50	10.70	0.345	67.2	0.70	638.4	3.47	1 : 2.02 : 10.01 : 15.94

TABLE 2

Analyses of silicomolybdotungstic acids

Acids	Weight of sample (in mg)	H_2O		Si		Mo		W		Ratio Si : Mo : W : H_2O
		(mg)	(mg-mole)	(mg)	(mg-mole)	(mg)	(mg-mole)	(mg)	(mg-mole)	
I	838.9	149.2	8.29	9.55	0.34	324.5	3.38	127.5	0.69	1 : 9.9 : 2.0 : 24
II	923.9	170.1	9.45	9.72	0.34	271.6	2.83	233.0	1.26	1 : 8.2 : 3.7 : 28
III	952.4	145.6	8.09	9.85	0.35	213.3	2.22	377.4	2.05	1 : 6.3 : 5.9 : 23
IV	870.0	147.3	8,18	8.06	0.29	117.6	1.22	403.7	2.19	1 : 4.2 : 7.5 : 28
V	990.2	152.3	8.46	8.40	0.36	60.1	0.62	555.5	3.01	1 : 2.0 : 10.0 : 28

Potentiometric titration. The prepared phosphomolybdotungstic acids were subjected to potentiometric titration, for which purpose 20 ml 0.02 M solution of each acid was taken, 20 ml distilled water was added, and titration carried out with 0.233 N KOH solution. Measurements were made on a potentiometer of the PPTV-1 type with a glass electrode and a tube amplifier of the LU-2 type. A calomel electrode was used for comparison. We rejected the use of the quinhydrone, hydrogen and hydroxyantimony indicator electrodes (for reasons given later) after a series of experiments. The temperature during the titration was held at 18°. For comparison we also titrated a mixture of phosphomolybdic and phosphotungstic diacids and of silicomolybdic and silicotungstic diacids in the ratio of 3 : 3. In Tables 3 and 4 are set forth the data obtained which characterize the titration jumps. The volumes of added alkali are converted in the tables to exactly 0.2 N concentration.

Constant potential at 18° was quickly established. In Fig. 1 the titration curves of acid III and a mixture of phosphomolybdic and phosphotungstic acids in equivalent amounts are compared.

Titration of acids with a central atom of silicon was at first undertaken under the same conditions as for acids with a central phosphorus atom. However, the addition of alkali after the first titration jump did not give good results. Constant potential at a pH greater than 4 was only established under the following conditions. After running in each portion of alkali, the solution was heated to the boil and then quickly cooled under the tap. The potential was measured at 18°. Without heating the reaction does not go to the end and the second titration jump is indefinite ("diffuse"), as well shown in Fig. 2, a.

TABLE 3

Potentiometric titration of phosphomolybdotungstic acids

0.2 N KOH (ml)	pH					Mixture of diacids P—Mo and P—W
	I	II	III	IV	V	
0	1.5	1.6	1.6	1.6	1.6	1.8
5.8	1.9	1.9	2.0	2.0	2.0	2.9
8.2	2.2	2.2	2.4	2.3	2.4	4.3
9.3	2.6	2.6	2.8	2.7	2.6	4.7
10.5	3.3	3.4	3.5	3.4	3.4	5.15
11.6	3.9	4.0	4.1	3.9	3.9	5.5
48.9	7.8	8.1	10.5	8.0	8.5	12.1
52.4	11.6	10.9	11.7	10.5	9.8	12.4
53.6	11.8	11.4	12.0	11.5	10.9	12.4

TABLE 4

Potentiometric titration of silicomolybdotungstic acids

0.2 N KOH (ml)	pH					Mixture of diacids (Si—Mo and Si—W)
	I	II	III	IV	V	
0	1.7	1.7	1.7	1.7	1.7	1.6
5.8	2.3	2.2	2.4	2.4	2.2	2.1
8.2	3.9	4.1	4.9	4.6	5.3	3.9
9.3	4.8	4.5	5.0	5.1	5.5	5.4
46.6	7.8	8.9	8.9	8.2	9.4	7.7
52.4	11.9	12.3	12.3	12.3	11.6	11.8
58.2	12.2	12.4	12.5	12.6	12.0	12.5

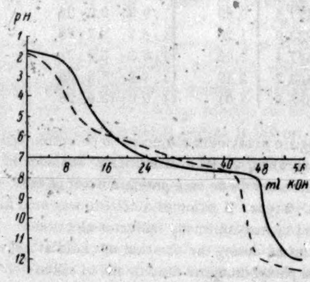

Fig. 1. Titration curves of phosphomolybdotungstic acid III (solid curve)and a mixture of diacids (broken curve).

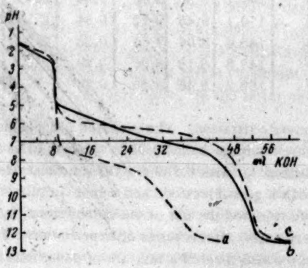

Fig. 2. Titration of silicomolybdotungstic acid III without heating (a); the same with preliminary heating (b); mixture of silicomolybdic and silicotungstic acids (c)

In Table 4 are set forth the results of measurements obtained with preliminary heating of the solution to the boil after running in the alkali and cooling.

In Fig. 2 are plotted the titration curves of acid III and of a mixture of silicomolybdic and silicotungstic acids in equivalent amounts.

Measurement of electrical conductivity. Measurements were made of the electrical conductivity of solutions of the synthesized heterotriacids and of their potassium salts. The starting solutions were prepared from the heteroacids. The weight of the sample was calculated so that 128 liters solution contained 1 g-mole. 50 ml of solution of each acid was prepared; solutions with correspondingly lower concentrations were obtained by successive dilution. Solutions of the potassium salts of the phosphomolybdic acids were obtained by adding to 25 ml of the starting acids an amount of KOH corresponding to 5 equivalents per mole acid; for salts of silicomolybdic acids the amount taken was 4 equivalents KOH per mole acid. The resistances of the solutions (R) were determined with the help of a special apparatus [8]. The constant of the apparatus was determined with a solution of chem. pure KCl. The temperature of the solutions was held at 25° ± 0.05 with the help of a TS-15 thermostat. The constant of the cell for measurement of the electrical conductivity was 0.535. Electrical conductivity was calculated from the formula $\frac{V \cdot 0.535}{R}$, where V is the dilution (number of liters of solution containing 1 g-mole substance).

In Table 5 and 6 are set forth the mean results of measurements expressed in reciprocal ohms.

TABLE 5

Electrical conductivity of phosphomolybdotungstic acids and their potassium salts

Dilution	Salts and acids			Acids		
	I	III	V	I	III	V
256	551	564	594	1459	1582	1699
512	584	620	656	1559	1650	1808
1024	670	679	728	1646	1712	1873
8192	–	–	–	1697	1901	2026

TABLE 6

Electrical conductivity of silicomolybdotungstic acids and their potassium salts

Dilution	Salts and acids			Acids		
	I	III	V	I	III	V
256	434	475	495	1397	1335	1305
512	496	513	520	1409	1348	1371
1024	528	561	553	1457	1420	1405

DISCUSSION OF RESULTS

Heterotriacids were synthesized with a central atom of phosphorus and silicon, with a varying but strictly definite composition of addends containing molybdenum and tungsten. The main conditions for such syntheses are: 1) Stoichiometric ratios of the components; 2) tungstate and molybdate must previously be converted into meta-compounds. This conversion was effected by gradual addition of the calculated amounts of HCl to the hot solution of the normal salts. Under these conditions tungstic acid is not precipitated, and the calculated amounts of tungsten and molybdenum enter completely into reaction. Our qualitative analyses of the aqueous phases (over the etherate) showed that they contain only insignificant amounts of tungsten and molybdenum.

The etherates are decomposed by addition of small amounts of water and careful removal of the ether by heating at 45-50° on a water bath. The phospho- and silicomolybdotungstic acids then crystallize out nicely. Determination of their composition (Tables 1 and 2) shows that the atomic ratios of P(Si): Mo: W in the synthesized compounds are close to the theoretical, namely: in acid I – 1: 10: 2; in acid II – 1: 8: 4; in acid III – 1: 6: 6; in acid IV – 1: 4: 8, and in acid V – 1: 2: 10.

The slight deviations from the calculated composition observed in the analytical results are explained by the difficulty of exact determination of tungsten in the form of WO_3 in presence of large amounts of molybdenum.

Potentiometric titration of the synthesized heterotriacids with varying content of molybdenum and tungsten with the aid of the glass electrode enables us to draw some important conclusions. Titration of phosphomolybdotungstic acids shows that their solutions contain not less than 5 salt-forming hydrogens, whereas the mixture of solutions of phosphomolybdic and phosphotungstic acids in various molar amounts contains 4 salt-forming hydrogens (Table 3). On the titration curve (Fig. 1) this corresponds to the first titration jump. The titration jump for acids with a central phosphorus atom is somewhat "drawn out" and does not give the possibility of sharp determination of the equivalent point. The first titration jump for silicomolybdotungstic acids is clearly manifested and exactly corresponds to 4 equivalents (Fig. 2). The second titration jump for all the synthesized acids corresponds to 24-25 equivalents. The reactions taking place can be represented by equations similar to the following equation for one of the acids:

$$H_7[P(Mo_2O_7)_3(W_2O_7)_3] + 26KOH \rightleftharpoons K_2HPO_4 + 6K_2MoO_4 + 6K_2WO_4 + 16H_2O.$$

The second titration jump corresponds to breakdown of the heterotriacids with separation of simple salts in the free states. On titration of a mixture of phosphomolybdic and phosphotungstic acids in equivalent amounts, this stage is reached at 22 equivalents of alkali, and for triacids at 24-25 equivalents, i.e. the breakdown reaction is reversible and does not go to completion. All the silicomolybdotungstic acids are fairly stable to strong caustic alkalies, and their decomposition in an alkaline medium only occurs on boiling.

Employment of the quinhydrone electrode did not give satisfactory results for detection of the second titration jump for all the synthesized acids since the second jump occurs in a strongly alkaline medium. The hydroxyantimony and hydrogen electrodes reduce all the phosphomolybdotungstic acids to "blue" immediately after their introduction. It is not without interest to note that silicomolybdic acid and its mixtures with silicotungstic acid are similarly reduced, whereas the triacids with a central silicon atom are not reduced.

The pH values of 0.02 molar solutions of phosphomolybdotungstic acids are 1.5-1.6, while the pH of the mixture of diacids is 1.8 and 1.9. Silicomolybdotungstic acids of the same concentration in solution have pH 1.7 and a mixture of the diacids of silicon 1.6. Measurements of the electrical conductivity of the synthesized heterotriacids I, III and V and of their potassium salts show that the conductivity of compounds with a central phosphorus atom is considerably higher than that of compounds with a central silicon atom. From the electrical conductivity of the salts we can infer that they dissociate to give approximately 6 and 5 ions. It may be suggested that dissociation of all the salts proceeds somewhat in accordance with the following equations:

$$K_5H_2[P(Mo_2O_7)_3(W_2O_7)_3] \rightleftharpoons 5K^+ + H_2[P(Mo_2O_7)_3(W_2O_7)_3]^{5-},$$

$$K_4H_4[Si(Mo_2O_7)_3(W_2O_7)_3] \rightleftharpoons 4K^+ + H_4[Si(Mo_2O_7)_3(W_2O_7)_3]^{4-}.$$

SUMMARY

1. Using as starting substances metatungstate or metamolybdate in stoichiometric amounts, isolation was effected in the free state of 10 heterotriacids with central phosphorus and silicon atoms and containing different ratios of molybdenum and tungsten.

2. On the basis of the Miolati-Rosenheim theory the analytical data enable formulas of the type of $H_7[P(Mo_2O_7)_n(W_2O_7)_m] \cdot xH_2O$ to be assigned to the compounds with a central phosphorus atom and of the type of $H_8[Si(Mo_2O_7)_n(W_2O_7)_m] \cdot xH_2O$ to the compounds with a central silicon atom, where $n + m = 6$, $x = 16-28$.

By means of potentiometric titration it was shown that salts of the composition $K_5H_2[P(Mo_2O_7)_n(W_2O_7)_m]$ and $K_4H_4[Si(Mo_2O_7)_n(W_2O_7)_m]$ are formed in solution; this was also confirmed by electrical conductivity measurements.

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PREPARATION OF SILICOTUNGSTIC ACID WITHOUT THE USE OF ETHER

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Silicotungstic acid is usually prepared from its sodium salt; a solution of the latter is extracted with ether in presence of inorganic acid for separation of the free acid [1]. Our problem was the development of a method of preparation of silicotungstic acid without the use of ether. Two methods were considered: 1) Direct synthesis of silicotungstic acid from silicic and tungstic acids; 2) synthesis of 8-substituted barium tungstate from various alkali salts of silicotungstic acid followed by decomposition of the barium silicotungstate with sulfuric acid and crystallization of the silicotungstic acids obtained.

Tungstic and silicic acids were prepared to test the possibility of obtaining heteropolyacids by reactions of silicic and tungstic acids according to the equation $12H_2WO_4 + H_2SiO_3 + xH_2O \rightleftharpoons H_8[Si(W_2O_7] \cdot xH_2O$ [2].

EXPERIMENTAL

In the experiments on direct synthesis we started from a weighed amount of tungstic acid (100 g), silicic acid in 500% excess of the amount calculated from the equation (converted to SiO_2), and 3 liters water.

The experiments did not give satisfactory results either when using relatively fresh tungstic acid (prepared 48 hours before synthesis) or aged tungstic acid gels (prepared 14 days before synthesis). The aged gels were even less satisfactory.

Subsequently we ran two experiments on direct synthesis of silicotungstic acid in an autoclave, using freshly precipitated tungstic acid.

Synthesis of the heteropolyacid was performed with continuous mechanical stirring under a pressure of 63.5 atm. and at a temperature of 165-200° in the autoclave jacket; each experiment lasted 6 hours; after discharging the autoclave, the solid phase was separated and the filtrate evaporated on a water bath; substantially no crystalline silicotungstic acid was obtained in either experiment.

Concerning 9-substituted barium silicotungstate. The literature data on barium salts of silicotungstic acid indicate that the salt least soluble in water is the 8-substituted $Ba_4[Si(W_2O_7)_6] \cdot xH_2O$. From the standpoint of our concepts on the basicity of heteropolyacids, this salt should exist as an independent chemical compound; the poor solubility in water would be expected to facilitate its removal from accompanying ions by washing, and the susceptibility to decomposition by sulfuric acid ought to lead to preparation of pure silicotungstic acid.

The literature on 8-substituted barium silicotungstate is scanty.

Marignac [3], the discoverer of the "isomeric" silicotungstic acids, was the first to describe 8-substituted barium cis-silicotungstate (a powder nearly insoluble in water). Treatment of the isomeric "trans-silicotungstic acid" with baryta water gave the 8-substituted "trans-silicotungstate" of barium in the form of a liquid which was oleaginous when hot and sticky and hard in the cold; on standing in the air, the liquid solidified to a glassy, brittle mass; in contact with water, the solid salt again became viscous. When the liquid barium "trans-silicomolybdate" is brought into contact with water, it changes into a white powder after a few days in the cold and more quickly on heating. The salt is almost insoluble in cold water but more soluble in boiling water. The glassy salt, after drying in the air at 100°, corresponds in composition to the nonahydrate; the powdery preparation obtained by prolonged contact of the liquid salt with hot water, contains 27 molecules of hydrate water.

The 8-substituted barium "trans-silicotungstate", first described by Marignac, was also obtained by Rosenheim and Jaenicke [4]. These authors started from the ammonium salt of the "trans-silicotungstic" acid which they treated with barium chloride. They obtained crystals containing 27 molecules of water.

Souchay [5] tried to disprove the high basicity of heteropolyacids, as indicated by the coordination theory.

Without any experimental data, he denied the existence of 8-substituted barium silicotungstate which had twice been described in the literature and carefully analyzed by Marignac and by Rosenheim and Jaenicke.

Synthesis of potassium silicotungstate, preparation from it of the 8-substituted barium salt and the free cis-silicotungstic acid. For the synthesis of barium silicotungstate, the preparation was first carried out of potassium silicotungstate; double decomposition of the latter with barium chloride gave 8-substituted barium silicotungstate, from which the free silicotungstic acid was isolated by treatment with sulfuric acid.

Preparation of potassium silicotungstate. A solution of ammonium paratungstate was heated with KOH on a water bath until NH_4^+ had been completely driven off (test with Nessler reagent); the liquid was then evaporated until the salt crystallized:

$$5(NH_4)_2O \cdot 12WO_3 + 10KOH = 5K_2O \cdot 12WO_3 + 10NH_4OH.$$

The yield of potassium paratungstate was 82%. Potassium silicotungstate was obtained from potassium paratungstate, potassium silicate and hydrofluosilicic acid according to the reaction: $5K_2O \cdot 12WO_3 + K_2SiO_3 + 4H_2SiF_6 = K_4H_4[Si(W_2O_7)]_6 + 4K_2SiF_6 + 2H_2O$.

Hydrofluosilicic acid was introduced at a temperature not exceeding 35° with hand stirring; the reaction mass was then heated to the boil and held 4 hours on the boiling water bath. Completion of the complex-formation reaction was checked by testing for $WO_4^{''}$ with hydrochloric acid. The solution of potassium silicotungstate, filtered from the excess of silicic acid and precipitated potassium fluosilicate, was evaporated until the liquid phase was barely present.

In experiments 4 and 5 (Table 1) potassium silicate was replaced by silicic acid; the latter proved more convenient since the potash water glass which was used in the investigation contained excess of free alkali and it was necessary to add excess of hydrofluosilicic acid to the reaction mixture.

TABLE 1

Results of experiments on the synthesis of potassium silicotungstate

Experiment number	Taken into reaction				Yield of potassium silicotungstate (hydrate) (in %)
	potassium paratungstate (containing 27 H_2O) (in g)	K_2SiO_3 (in ml) or H_2SiO_3 (in g) converted to equivalent SiO_2	H_2O (in l)	20% H_2SiF_6 (in g)	
		K_2SiO_3 (d 1.27)			
1	75	63	1.75	34	75.0
2	150	125	2.5	100	69.0
3	170	150	2.8	185	75.5
		H_2SiO_3			
4	50	5.6	0.8	50	78.5
5	130	16	2.0	65	Crystalline salt not separated

As the investigation showed, the synthesis of potassium silicotungstate from silicate and paratungstate in presence of excess of hydrofluosilicic acid (5-6 moles) led to formation of salts with greater acidity than 4-substituted salts; attempts to isolate the free silicotungstic acid by removal with hydrofluosilicic acid of the potassium ion of the silicotungstate led only to formation of more acidic salts (1-3-substituted) and to a process of breakdown of the heteropoly anion $[Si(W_2O_7)_6]^{VIII}$. These observations are fully consistent with the results of earlier studies by Marignac [6], Brandhorst and Kraut [7], A. V. Rakovsky [8], E. A. Nikitina and A. S. Kokurina [9].

The optimum concentration of hydrofluosilicic acid is 2-3 moles per mole of potassium paratungstate at a concentration of the latter salt of 40-60 g; in this case the 8-substituted potassium salt of silicotungstic acid is formed. Actually, judging by the very high solubility of the potassium silicotungstate obtained in the reaction, we were dealing with highly substituted salts of silicotungstic acid, as was also confirmed by the analyses presented in Table 2.

TABLE 2

Results of analysis of potassium silicotungstate (Experiments 3 and 4, Table 1)

Substance	Composition of potassium silicotungstate (in %)	
	experiment 3	experiment 4
H_2O	10.30	10.00
SiO_2 •	2.00	1.50
K_2O •	11.34	14.00
Calculated	The 8-substituted salt contains 10.83% K_2O	8-Substituted salt admixed with K_2O

• SiO_2 and K_2O recalculated to the anhydrous composition.

The solution of potassium silicotungstate obtained in experiment 5 (Table 1) was filtered from excess silicic acid and treated with 25% barium chloride solution in the amount needed for formation of the 8-substituted salt $Ba_4[Si(W_2O_7)_6] \cdot xH_2O$; as soon as the first portions of barium chloride solution had been added, a heavy, yellowish oil was formed which changed to a white crystalline mass after 1 $^1/_2$ - 2 hours. Addition of the last portions of barium chloride solution was accompanied by separation of a finely crystalline, white, fairly voluminous precipitate which was separated from the crystals settling at the bottom of the dish. Each fraction of barium salt was pressed separately and then treated with sulfuric acid (1 : 1); after separation from the barium sulfate, the solution of silicotungstic acid was evaporated for crystallization; microscopic examination of the crystals revealed the formation of silicotungstic acid in one and the same cis-form.

Formation of oily barium salts is characteristic of "trans-silicotungstic" acid; evidently in the process of precipitation with barium chloride two "isomeric" barium salts are formed; on further standing the labile "trans-form" of the salt is converted into the more stable cis-form, i.e. the cis-silicotungstic acid whose preparation was the subject of our investigation.

In some experiments barium silicotungstate was obtained by the action of barium hydroxide upon a solution of potassium silicotungstate; the precipitates formed by the action of barium hydroxide differed in crystal form from those obtained by the action of barium chloride; it was also observed that not every addition of barium chloride led to appearance of a heavy oil of the 8-substituted barium salt.

In order to elucidate the difference between the barium salts formed, analyses were performed on the barium silicotungstates obtained by the two methods (Table 3).

TABLE 3

Results of analysis of barium silicotungstates obtained by the action of different precipitants

Substance	Precipitant $Ba(OH)_2 \cdot 8H_2O$	Precipitant $BaCl_2 \cdot 2H_2O$			Calculated for the anhydrous 8-substituted salt
	salt 1	salt 2	salt 3	salt 4	
	content (in %)				
H_2O	5.0	11.0	11.00	9.80	–
SiO_2	0.7	1.9	1.84	1.90	1.73
WO_3	70.3	80.3	82.36	81.02	80.57
BaO	29.0	17.8	15.80	17.08	17.70

Note. Content of components of salt recalculated for anhydrous salt. The WO_3 content is given by difference.

The results of the analyses show that barium hydroxide gave a salt with a higher content of barium oxide; treatment with barium chloride gave preparations whose compositions were close to that of the 8-substituted salt of silicotungstic acid. The solubility of both salts was identical — 0.03 wt.-% at 20°.

Decomposition of both salts by sulfuric acid invariably leads to formation of cis-silicotungstic acid; its yield, however, is higher in the case of employment of barium silicotungstate free from excess of BaO.

In the isolation of barium silicotungstate from solutions of potassium salts (at a ratio of 1 : 1.5, 1 : 2) with barium chloride, the yield of $Ba_4[Si(W_2O_7)_6] \cdot xH_2O$ is 69.5-79.3%. The well-washed, not thoroughly dried, hydrated form of the salt is easily decomposed by sulfuric acid; complete elimination of the barium ion necessitates very careful addition of H_2SO_4, since excess of the latter at the stage of evaporation of the solution leads to partial decomposition of the preparation.

Calculation of the amount of sulfuric acid needed for decomposition of barium tungstate is based upon the weight of barium chloride taken for precipitation of the $[Si(W_2O_7)_6]^{VIII}$ ion. After addition of about 4/5 of the calculated amount of sulfuric acid, it is necessary to make check tests for the presence of $SO_4^{=}$ (10% $BaCl_2$) and for the presence of still undecomposed barium salt (10% H_2SO_4). Precipitation is effected by stirring with 50% sulfuric acid, after which the solution is diluted approximately twofold, stood for 2 hours and again tested for content of Ba and $SO_4^{=}$ ions.

In Table 4 are set forth the results of experiments on the preparation of silicotungstic acid from potassium silicotungstate with conversion of the latter into the 8-substituted barium salt.

TABLE 4

Data on the preparation of silicotungstic acid from the potassium salt via the barium salt

Expt. Number	Conditions of purification of barium salt	Results of analysis of silicotungstic acid (hydrate) (in %)			
		H_2O	SiO_2	K_2O	WO_3
1	Barium salt not washed free from Cl	14.9	1.98	1.02	82.12
2	Ditto	5.9	2.20	1.06	–
3	Barium salt washed until the wash liquors were weakly opalescent	16.0	2.06	0.60	–
4	Barium salt washed until the aqueous extract from the salt had fain opalescence	16.00	2.26	0.02	81.72
5	Ditto	17.3	1.98	0.06	80.66
6	Ditto	8.2	1.94	0.015	89.85
7	Acid from preceding experiment after washing on filter	13.7	1.94	0.4	83.96

These experiments show that after careful washing of the barium silicotungstate, a heteropolyacid is obtained with a negligible content of potassium salt; washing of silicotungstic acid with water on the filter increases its content of potassium ions due to the higher solubility of the heteropolyacid in comparison with the potassium chloride.

Preparation of barium silicotungstate and silicotungstic acid from sodium paratungstate

In a first series of experiments, sodium paratungstate was prepared from ammonium paratungstate by heating a solution of the latter with NaOH; in other respects the preparation of sodium silicotungstate and preparation from the latter of the barium salt were carried out on the same lines as for potassium silicotungstate except that hydrochloric acid (d 1.095) was employed for acidification.

125 g ammonium paratungstate was dissolved in 1.5 liters water, and addtion was made of 35 ml 40% sodium hydroxide solution and of silicic acid in 450% excess; complex formation proceeded at pH 0.4 (colorimetric determination).

In another series of experiments sodium paratungstate was prepared from sodium tungstate by treating its solution with hydrochloric acid (d 1.12) until a weakly alkaline or neutral reaction (pH 7-7.) was obtained at the boiling point; the barium salt was obtained by precipitation of a solution of sodium silicotungstate with a 25% solution of barium chloride. We may point out that in all the synthesis experiments we did not isolate sodium silicotungstate in the crystalline form, but the $[Si(W_2O_7)_6]^{VIII}$ ion was precipitated by the barium ion directly from the solution on completion of the reaction of complex formation.

Analysis of the barium salt showed that a preparation of the 7-substituted salt admixed with 8-substituted salt had been obtained.

Found %: H_2O 11.00; SiO_2 1.52; BaO 16.00.

The prepared barium silicotungstates were treated with sulfuric acid; the specimens of silicotungstic acid were examined under the microscope and analyzed.

Found %: H_2O 8-17; SiO_2 1.98-2.2; alkali salts recalculated for Me_2O 0.2-0.02; $SO_4^{=}$ 0.05-0.07.

A solution of silicotungstic acid in water (1 : 20) should be transparent; in the event of a cloudy solution being obtained, it must be heated to 80-90° and should then remain transparent even on cooling.

Synthesis of ammonium silicotungstate, preparation from it of the barium salt and of free cis-silicotungstic acid

The first experiment was performed with a solution of ammonium paratungstate to which was added an excess of H_2SiO_3; HCl was used for acidification; complex formation was not observed at a pH of the reaction medium of 0.4, but tungstic acid was precipitated. At a lower acidity of the solutions (pH 1.4-1.5) formation of the silicotungstate ion proceeded normally; it was experimentally established that the optimum concentration of ammonium paratungstate solution for the synthesis was 1 : 12.

A freshly precipitated silicic acid gel and 30 ml of hydrochloric acid (d 1.095) were added to a solution of ammonium paratungstate (1 : 12); the resulting solution was heated for 2-3 hours to effect the reaction of complex-formation, and then held at room temperature for 10-15 hours; the precipitate of silicic acid was filtered off, washed with water and the filtrate and wash water were evaporated down to d 1.2-1.3 (at 50°); after this, barium silicotungstate was precipitated with barium chloride solution; the experiment showed that precipitation of $[Si(W_2O_7)_6]^{VIII}$ with barium chloride from more dilute solutions did not permit complete precipitation of the heteropolyanion (Table 5). Further isolation of barium silicotungstate and its decomposition with sulfuric acid were performed as described above.

TABLE 5

Preparation of barium silicotungstate and silicotungstic acid from ammonium paratungstate. Experimental conditions: ammonium paratungstate 250 g, H_2O 0.550 liter, 25% $BaCl_2 \cdot 2H_2O$ 300 ml

Preparation number	Barium salt obtained (in %)	Yield of silicotungstic acid (in %)
1	77	31-39 (first fraction)
2	72	
3	77	
4	65.7	
5	78.5	
6	77	

As the microscopic and analytical examinations showed, the preparations did not differ from those described in the preceding series of experiments in respect of content of SiO_2, H_2O and alkali salts (Table 4).

On evaporation of the filtrates, the yield of silicotungstic acid reaches 60-70%. We observed the process of formation of $[Si(W_2O_7)_6]^{VIII}$ in solutions of potassium, sodium and ammonium paratungstates at various values of pH. The differing acidities of the salt solutions are evidently associated with the fact that the original polybasic acid $H_{10}[H_2(WO_4)_6]$, from which the paratungstates are formed, the hydrogen ions are replaced by bases of different strengths, in consequence of which the pH of the solutions of alkali metal paratungstates varies; hence the synthesis of the silicotungstate anion also proceeds at various values of pH.

ANALYTICAL

The water content is determined by thorough drying of a weighed sample at about 100° followed by calcination to constant weight. SiO_2 and alkali metals are determined by hydrochlorination of a weighed sample of the dehydrated and calcined preparation in a tube furnace at 750° for removal of tungsten.

The residue after hydrochlorination is treated with water and filtered from SiO_2; the latter is calcined and weighed; ions of barium or alkali metals in the filtrate are determined by the usual methods.

SUMMARY

1. The possibility was tested of direct synthesis of silicotungstic acid from tungstic and silicic acids; the experiments were a failure.

2. A method was developed for the preparation of 8-substituted barium silicotungstate from potassium, sodium and ammonium silicotungstates.

3. The applicability of the coordination theory to the problem of evaluation of the basicity of heteropolyacids was confirmed.

4. A procedure was given for decomposition of barium silicotungstate with sulfuric acid for isolation of the free cis-silicotungstic acid.

5. A study was made of the composition of the barium silicotungstates isolated by the action of barium chloride and barium hydroxide upon alkali silicotungstates.

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• T. p. = C. B. Translation pagination.

AMMONIUM-CALCIUM OCTOBORATE

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Alkaline earth metals form characteristic double borates of the type of $Me_2O \cdot Me^{II}O \cdot 4B_2O_3$ aq. Such octoborates have been obtained with potassium in the case of calcium, strontium and barium [1-3]. It was found that their potassium ion can be replaced by the ammonium ion. Double octoborates of sodium and the alkaline earth metals have not hitherto been obtained. Ammonium-calcium octoborate is formed in alkaline solution (pH 9.8) in the reaction of calcium and ammonium ions with the borate anion according to the equation:

$$CaCl_2 + 2(NH_4)_2B_4O_7 + aq \longrightarrow (NH_4)_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O + 2NH_4Cl.$$

On bringing into contact solutions of calcium chloride and ammonium tetraborate, an amorphous precipitate comes down which only gradually becomes crystalline. Mixing of the solutions is accompanied by a rapid rise in pH from 5 to 9.8. Under such conditions a mixture of various borates comes down becaue, as investigations showed [4], each borate is formed in a relatively narrow pH range. Constancy of pH in this reaction is ensured by a large excess of ammonium tetraborate. Crystallization of the precipitate only sets in at a ratio of reactants of 1 : 4, and even then only after 20 hours. On increasing the amount of ammonium tetraborate, crystallization of the precipitate starts in 2 hours. Ammonium tetraborate can be replaced by corresponding proportions of boric acid and concentrated ammonia solution.

EXPERIMENTAL

Synthesis of $(NH_4)_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$. 12 g boric acid was dissolved in 200 ml water and 17.5 ml concentrated ammonia solution was added. 2.2 g $CaCl_2 \cdot 6H_2O$ was dissolved in 20 ml water. On mixing the solutions a white amorphous precipitate came down and crystallized completely after 3 days. The crystals were collected and washed with alcohol and ether. Yield 19 g. The crystals are transparent and 0.1-2.0 mm in size; they are perfectly stable in the air and do not change in composition when kept. The following chemical analysis of 4 specimens (I-IV) shows that their composition corresponds to the formula $(NH_4)_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$ (Table 1).

TABLE 1

	Found (in %)				Calculated (in %)
	I	II	III	IV	
$(NH_4)_2O$	8.65	8.70	8.57	8.62	8.64
CaO	9.14	9.26	9.38	9.34	9.30
B_2O_3	46.03	46.27	46.33	46.15	46.20
H_2O	35.97	35.69	35.92	35.84	35.86
Total	99.79	99.72	100.20	99.95	100.0

Pycnometric determination of the density of the crystals in toluene gave a value of d^{25} 1.650 g/ml.

Dehydration of the preparation was effected by slow heating of 1 g of the substance in a crucible furnace to constant weight at a specified temperature which was established from thermographic data. At 50° ammonium-calcium octoborate loses 1 mole water. Starting at 80° water goes off together with 1 mole ammonia, and the preparation loses 9 moles water. At 110° the preparation loses still another mole of water (the tenth) and evolution of a second molecule of ammonia continues. The latter process is prolonged to 600°. The last two moles of water are slowly lost on heating to 420°.

Three endothermic effects are visible on the thermograms of ammonium-calcium octoborate (Fig. 1): at 88, 110 and 429°; there is also an exothermic effect between 639 and 695°. The first endothermic effect at 88° is associated with the loss of 1 mole ammonia and part of the crystal water; the second at 110° is evidently associated with the loss of 10 moles crystal water. The third effect at 429° is bound up with the loss of the last two molecules of water. It follows both from the dehydration data and from the thermograms that two moles of water are especially firmly retained. The endothermic effect between 639 and 695° no longer relates to ammonium-calcium octoborate (since ammonia has already been lost), but is apparently associated with a recrystallization of the residual calcium borate.

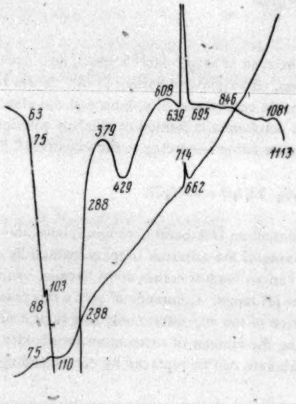

Fig. 1. Thermogram of ammonium-calcium octoborate.

TABLE 2

Spherical coordinates of crystals of ammonium-calcium octoborate

Symbol	Measured φ	Measured ρ	Calculated φ	Calculated ρ
100	7'	90°	0°	90°
010	89°54'	90°	90°	90°
110	37°1'	90°	–	–
011	90°	35°2'	–	–
111	37°12'	49°5'	37°1'	49°21'

Examination of the crystals in polarized light in all three directions reveals that they have right extinction; this, in conjunction with other evidence, demonstrates that they belong to the rhombic system. Results of crystal measurements in a two-circle reflecting goniometer are set forth in Table 2.

It follows from the measurements that the crystals possess a center of symmetry, 3 axes of symmetry of the second order and 3 planes of symmetry, and that they belong to the rhombic-bipyramidal class. In shape they are a combination of two pinacoids {100}, {010}, two prisms {110}, {011}, and a bipyramid {111} (Fig. 2).

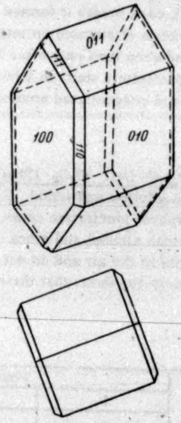

Fig. 2. Crystals of ammonium-calcium octoborate.

The ratio of the crystallographic axes was calculated from the spherical coordinates of the 110 and 011 faces: $a_0 : b_0 : c_0 = 0.7538 : 1 : 0.7010$.

For approximate determination of the parameters of the unit cell of ammonium-calcium octoborate crystals, rotating crystal X-ray diagrams were prepared for the directions [100], [010] and [001]. The identity periods were calculated from the distances between the planes; the following results were obtained: $a = 12.55$ A, $b = 16.70$ A and $c = 11.65$ A.

The following data were calculated from the parameters of the unit cell found: 1) ratio of the roentgenographic axes — $a : b : c = 0.7515 : 1 : 0.6976$; from this the ratio of the goniometric axes to the roentgenographic axes: $a_0 : b_0 : c_0 = a : b : c$; 2) volume of the unit cell — $v = a \cdot b \cdot c = 2441.67\ A^3$; 3) number of molecules in unit cell — $z = \frac{vdN}{M} = \frac{2441.67 \cdot 1.650 \cdot 0.602}{602.912} = 4.02 \approx 4.$

SUMMARY

1. A method is proposed for the preparation of ammonium-calcium octoborate as well-formed crystals suitable for crystallographic and X-ray investigations. Their chemical composition corresponds to the formula $(NH_4)_2O \cdot CaO \cdot 4B_2O_3 \cdot 12H_2O$.

2. Thermograms are plotted and the process of dehydration is studied.

3. Crystals of ammonium-calcium octoborate belong to the rhombic-bipyramidal class.

The parameters of the unit cell of crystals of ammonium-calcium octoborate are determined.

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IRREVERSIBLE RECIPROCAL SYSTEMS OF THE SINGLUAR TYPE WITH LAYERING FROM CHLORIDES AND NITRATES OF POTASSIUM AND SILVER, AND BROMIDES AND NITRATES OF POTASSIUM AND SILVER

G. M. Lifshits

Double decomposition of silver nitrate with potassium halides has already been studied in part [1, 2, 6].

All the authors report a sharp displacement of the equilibrium reaction in the direction of formation of silver halides due to their insolubility in fused potassium nitrate and to the high thermal effect of the reactions:

$$AgNO_3 + KCl \longrightarrow AgCl + KNO_3 + 14.63 \text{ kcal/equiv.}$$

$$AgNO_3 + KBr \longrightarrow AgBr + KNO_3 + 18.43 \text{ kcal/equiv.}$$

in which connection these systems, according to the classification of A. G. Bergman and N. S. Dombrovskaya, may be classed as singular, reciprocal-irreversible systems.

The character of the complete fusion diagrams of the reciprocal systems $K, Ag \| Cl, NO_3$ and $K, Ag \| Br, NO_3$ studied by us, confirms their singularity.

EXPERIMENTAL

The systems were studied by the visual-polythermal method of physico-chemical analysis. The temperature of the melts was measured with a nichrome-constantan thermocouple. Melting was performed in glass test tubes and the melt was stirred with a glass stirrer. Separation of the first crystals was observed before 600°.

The starting salts KNO_3, KCl, KBr, $AgNO_3$ were recrystallized from chemically pure reagents; AgCl and AgBr were synthesized. The melting points of the pure salts were respectively: 337, 774, 740, 208, 452, 419°. All the percentages given are molar.

Binary Systems •

1. System KNO_3-KCl [3, 1, 4]; eutectic point at 320° and 6% KCl. Transition point (melting with decomposition of the compound $KNO_3 \cdot KCl$) at 360° and 17.4% KCl.

2. System KNO_3-KBr [1]; eutectic point at 336° and ~0.7% KBr. Transition point (melting with decomposition of the compound $KNO_3 \cdot KBr$) at 342° and 4.5% KBr.

3. System $AgNO_3-KNO_3$ [1]; eutectic point at 131° and 38% KNO_3. Transition point (melting with decomposition of the compound $AgNO_3 \cdot KNO_3$) at 134° and 45.5% KNO_3. Polymorphic transformation of $AgNO_3$ at 162°.

4. System $AgNO_3-AgCl$ [1, 4]; eutectic point at 176° and 18.5% AgCl. Transition point (compound $AgNO_3 \cdot AgCl$) at 200° and 31% AgCl.

5. System $AgNO_3-AgBr$ [1]; eutectic point at 155° and 24% AgBr. Transition point (compound $AgNO_3 \cdot AgBr$) at 188° and 45.5% AgBr.

• All the binary systems were repeated by us.

6. System AgCl–KCl [1, 4, 5]; eutectic point at 318° and 30% KCl.

7. System AgBr–KBr [1]; eutectic point at 286° and 31% KBr.

System K, Ag // Cl, NO_3

For elucidation of the character of the interaction inside the reciprocal system and of the surface of the liquidus, a study was made of 2 diagonal sections and 16 internal cuts, * extending in various directions.

Diagonal sections. The fusion diagram of the stable diagonal section of KNO_3–AgCl (Fig. 1) consists of two horizontal lines corresponding to the melting points of AgCl (452°) and KNO_3 (337°), demonstrating the substantially complete immiscibility of the components of the stable pair in the fused state.

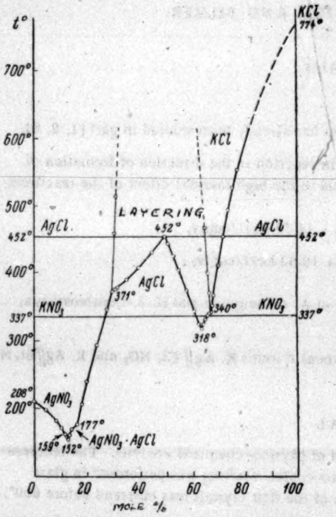

Fig. 1. Diagonal sections of the system K, Ag // Cl, NO_3.

The unstable diagonal section of $AgNO_3$–KCl indicates the double decomposition of the reciprocal system K, Ag // Cl, NO_3. The fusion diagram of the unstable section (Fig. 1) has the character of a binary system and consists of four crystallization branches: $AgNO_3$, $AgNO_3 \cdot AgCl$, AgCl, KCl, which intersect respectively at 152° and 12.5% KCl, 177° and 16.5% KCl, 318° and 63.5% KCl. A polymorphic transformation is observed at 159° on the $AgNO_3$ crystallization branch. The layering region is located in the interval from 30% KCl at 371° to 67% KCl at 340°.

On the silver chloride crystallization branch of the unstable diagonal and of all the internal cuts, the formation is observed of singular points on the ordinates corresponding to the composition of the stable diagonal at 452°.

The results of all the investigations are generalized in the fusion diagram in the form of an orthogonal projection of the isotherms of the concentration square of the reciprocal system (Fig. 2).

The diagram of the surface of the liquidus of the system K, Ag // Cl, NO_3 is characterized by seven fields of crystallization; their areas in percentages of the total area of the square are: AgCl 66.15, KCl 27.59, $AgNO_3$ 3.80, compounds $AgNO_3 \cdot AgCl$ 2.17, compounds $AgNO_3 \cdot KNO_3$ 0.09, compounds $KNO_3 \cdot KCl$ 0.18, KNO_3 0.02. In the field of crystallization of $AgNO_3$ was observed a line of polymorphic transformation of silver nitrate at 159°.

All the fields of crystallization meet in four nonvariant points (Table 1).

TABLE 1

Points	Characteristics of points	temperature	Composition (in mole %)				Equilibrium phases
			$AgNO_3$	KNO_3	AgCl	KCl	
E_1	Eutectic	113°	59.5	37.7	2.80	–	$AgNO_3 + AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgCl$
E_2	Ditto	315	–	94.0	0.39	5.61	$KNO_3 + KNO_3 \cdot KCl + AgCl$
P_1	Transition	122	57.4	40.2	2.40	–	$AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgCl + AgCl$
P_2	Ditto	317.5	–	81.0	3.60	15.4	$KNO_3 \cdot KCl + KCl + AgCl$

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* In view of the great mass of data, the data for the internal cuts are not given.

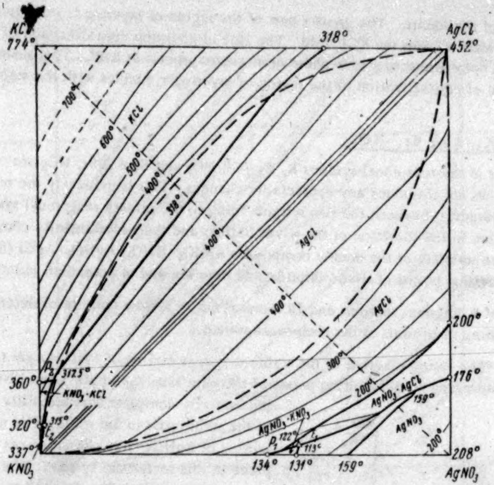

KCl
774°
318°
AgCl
452°
700°
600°
500°
400°
318°
KCl
400°
AgCl
400°
AgCl
300°
200°
200°
$AgNO_3 \cdot AgCl$
176°
159°
P_3
312.5°
360°
$KNO_3 \cdot KCl$
320°
315°
E_2
$AgNO_3 \cdot KNO_3$
P_1
122°
E_1
113°
$AgNO_3$
200°
337°
KNO_3
134°
131°
159°
208°
$AgNO_3$

Fig. 2. Fusion diagram of the system K, Ag//Cl, NO_3.

The position of the nonvariant points and of the lines of common crystallization of the components is given in the form of projections of these points and of the lines of the ternary system $KNO_3-AgCl-AgNO_3$ on to the $AgNO_3-KNO_3$ side (Fig. 3) and of the ternary system $KNO_3-AgCl-KCl$ on to the KNO_3-KCl side (Fig. 4).

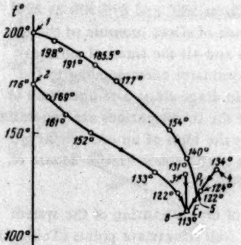


Fig. 3. Projection of the lines of common crystallization of the ternary system K, Ag//Cl, NO_3 on to the $AgNO_3-KNO_3$ side.

1) $AgNO_3 \cdot AgCl + AgCl$, 2) $AgNO_3 + AgNO_3 \cdot AgCl$, 3) $AgNO_3 + KNO_3 \cdot AgNO_3$, 4) $KNO_3 \cdot AgNO_3 + KNO_3$, 5) $AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgCl + AgCl$, 6) $AgNO_3 + AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgCl$.

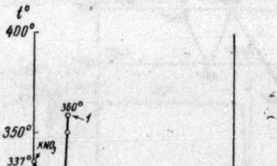


Fig. 4. Projection of the lines of common crystallization of the ternary system K, Ag//Cl, NO_3 on to the $KCl-KNO_3$ side.

1) $KNO_3 \cdot KCl + KCl$, 2) $KNO_3 + KNO_3 \cdot KCl$, 3) $KNO_3 \cdot KCl + AgCl + KCl$, 4) $KNO_3 + KNO_3 \cdot KCl + AgCl$, 5) $AgCl + KCl$.

The stable KNO_3-AgCl diagonal is a rectilinear singular ridge and divides the square of the reciprocal system into two ternary systems: $KNO_3-AgCl-AgNO_3$ and $KNO_3-AgCl-KCl$.

The region of layering is in the form of an oval whose major axis passes through the stable diagonal; it occupies 52% of the area of the square. The greater part of the region of layering is contiguous with the AgCl crystallization field and partly adjoins the KCl field. The line of common crystallization of these salts is in the region of layering and corresponds to a four-phase monotectic process at 318°. The node corresponding to the maximum temperature of crystallization in the region of layering coincides with the stable diagonal of KNO_3-AgCl.

Reciprocal system K, Ag||Br, NO_3

The fusion diagrams of the reciprocal systems K, Ag||Cl, NO_3 and K, Ag||Br, NO_3 are very similar; replacement of Cl' by Br' does not introduce any appreciable changes. This is evidently the result of the complete similarity (in form and character) between the two systems forming the ternary reciprocal systems; of the conspicuous shift of the reaction in the direction of the silver halides and their substantially complete insolubility in potassium nitrate; of the stability of the double compounds $AgNO_3 \cdot KNO_3$, $AgNO_3 \cdot AgCl$ (Br), $KNO_3 \cdot KCl$ (Br) and the closeness of the melting points of silver chloride and bromide and of potassium chloride and bromide.

A study was made of 2 diagonal sections and 18 internal cuts • for the purpose of determination of the surface of primary separations of crystals of the reciprocal system.

Diagonal sections. The fusion diagram of the stable diagonal section of KNO_3-AgBr (Fig. 5) consists of two horizontal lines corresponding to the melting points of the pure salts AgBr (419°) and KNO_3 (337°), indicating substantially complete immiscibility of the components of the stable pair in the melt. The unstable diagonal section of $AgNO_3-KBr$ characterizes the reaction taking place in this reciprocal system. The fusion diagram of the unstable section (Fig. 5) consists of 4 branches of crystallization: $AgNO_3$, $AgNO_3 \cdot AgBr$, AgBr and KBr, which intersect respectively at 142° and 14% KBr, 169° at 21% KBr, 335° at 59% KBr.

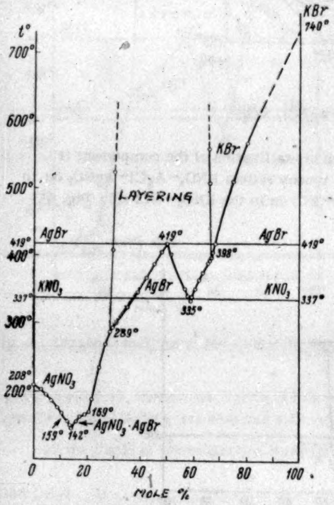


Fig. 5. Diagonal sections of the system K, Ag||Br, NO_3.

On the $AgNO_3$ crystallization branch is observed a very slight discontinuity corresponding to the polymorphic transformation at 159°. Layering occurs in the interval between 29% KBr at 289° and 67% KBr at 398°. The crystallization branch of silver bromide of the unstable diagonal sections and all the internal cuts have a singular point on the ordinates corresponding to the composition of the stable diagonal at a temperature of 419°. The results of all the investigations are generalized in the fusion diagram in the form of an orthogonal projection of the isotherms of the concentration square of the reciprocal system (Fig. 6).

The seven fields of crystallization of the system K, Ag||Br, NO_3 meet in four nonvariant points (Table 2). The areas of the field of crystallization in percentages of the total area of the square are: AgBr 59.043, KBr 32.193, $AgNO_3$ 4.312, compound $AgNO_3 \cdot AgBr$ 4.372, compound $AgNO_3 \cdot KNO_3$ 0.062, compound $KNO_3 \cdot KBr$ 0.014, KNO_3 ~0.005 (substantially insignificant).

TABLE 2

Points	Characteristics of points	Temperature	Composition (in mole %)				Equilibrium phases
			$AgNO_3$	KNO_3	AgBr	KBr	
E_1	Eutectic	119°	61.10	37.00	1.90	–	$AgNO_3 + AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgBr$
E_2	Ditto	322	–	99.50	0.10	0.40	$KNO_3 + KNO_3 \cdot KBr + AgBr$
P_1	Transition	127	57.76	40.41	1.84	–	$AgNO_3 \cdot KNO_3 + AgNO_3 \cdot AgBr + AgBr$
P_2	Ditto	331	–	96.00	0.42	3.58	$KNO_3 \cdot KBr + AgBr + KBr$

• Data for the internal cuts are omitted.

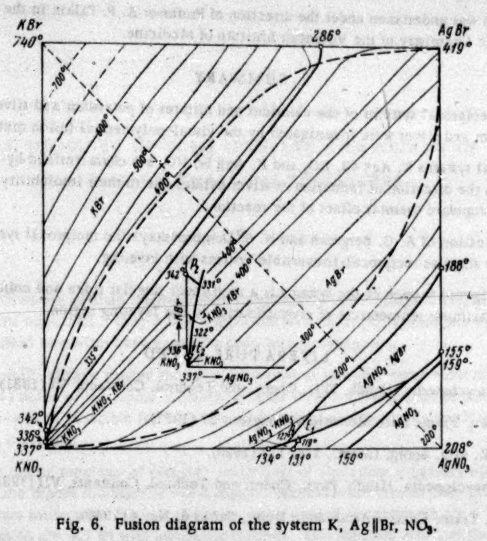
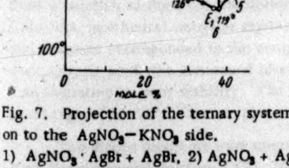

KBr
740°
286°
AgBr
419°
700°
600°
500°
400°
KBr
188°
P₂
342°
331°
KNO₃·KBr
AgBr
322°
E₂
335°
336°
KNO₃
337° — AgNO₃
300°
200°
155°
159°
AgNO₃·AgBr
AgNO₃
KNO₃·KBr
KNO₃
342°
336°
337°
KNO₃
AgNO₃·KNO₃
127°
E₁
119°
134°
131°
159°
208°
AgNO₃

Fig. 6. Fusion diagram of the system K, Ag‖Br, NO$_3$.

The position of the nonvariant points and of the lines of common crystallization of the components is given in the form of projections of these points and lines of the ternary system KNO$_3$—AgBr—AgNO$_3$ on to the AgNO$_3$—KNO$_3$ side (Fig. 7) and of the ternary system KNO$_3$—AgBr—KBr on to the KNO$_3$—KBr side (Fig. 8).



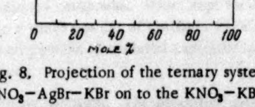


Fig. 7. Projection of the ternary system K, Ag‖NO$_3$, Br on to the AgNO$_3$—KNO$_3$ side.
1) AgNO$_3$ · AgBr + AgBr, 2) AgNO$_3$ + AgNO$_3$ · AgBr, 3) AgNO$_3$ + AgNO$_3$ · KNO$_3$, 4) AgNO$_3$ · KNO$_3$ + KNO$_3$, 5) AgNO$_3$ · KNO$_3$ + AgNO$_3$ · AgBr + AgBr, 6) AgNO$_3$ + + AgNO$_3$ · KNO$_3$ + AgNO$_3$ · AgBr.

Fig. 8. Projection of the ternary system KNO$_3$—AgBr—KBr on to the KNO$_3$—KBr side.
1) KNO$_3$ + KNO$_3$ · KBr, 2) KNO$_3$ · KBr + + KBr, 3) KNO$_3$ · KBr + KBr + AgBr, 4) KNO$_3$ + + KNO$_3$ · KNO$_3$ · KBr + AgBr, 5) KBr + AgBr.

The stable diagonal section is a rectilinear singular ridge and divides the square of the reciprocal system into two ternary systems: KNO$_3$—AgBr—AgNO$_3$ and KNO$_3$—AgBr—KBr.

The layering region has the form of an oval passing across the stable diagonal, and occupies 54% of the area of the square. The nonvariant line of common crystallization of AgBr and KBr passes through the layering region and corresponds to the four-phase monotectic process at 335°

The node corresponding to the maximum temperature of crystallization in the layering region coincides, as in the case of the system K, Ag‖Cl, NO_3, with the stable diagonal.

The investigation was undertaken under the direction of Professor A. P. Palkin in the laboratory of the Department of Inorganic Chemistry of the Voronezh Institute of Medicine.

SUMMARY

1. The ternary reciprocal systems of the chlorides and nitrates of potassium and silver and the bromides and nitrates of potassium and silver were investigated by the visual-polythermal fusion method.

2. The reciprocal systems K, Ag‖ Cl, NO_3 and K, Ag‖ Br, NO_3 are characterized by a sharp shift of the equilibrium reaction in the direction of formation of silver halides due to their insolubility in fused potassium nitrate and to the high standard thermal effect of the reaction.

3. In the classification of A. G. Bergman and N. S. Dombrovskaya the reciprocal systems K, Ag‖Cl, NO_3 and K, Ag‖Br, NO_3 are singular reciprocal-irreversible systems with layering.

4. The stable diagonal section of the systems is a rectilinear singular ridge and coincides with the node corresponding to the maximum temperature of crystallization in the layering region.

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Voronezh State Zooveterinary Institute

DIPOLE MOMENTS OF SOME COMPLEX COMPOUNDS OF INDIUM AND THALLIUM TRIHALIDES

I. A. Sheka

Trihalides of metals of the gallium subgroup form considerably fewer complex compounds than halides of compounds of boron and aluminum. Only a few compounds of thallium trichloride are described in the literature, and their physical properties have generally been little investigated.

A number of authors [1-4] have studied the polar properties of complex compounds of aluminum halides. Determinations have been made of the dipole moments of some complex compounds of boron [1, 2, 5] and of gallium [6]. No data have been available for the dipole moments of complex compounds of the remaining elements of the gallium subgroup.

Comparison of the dipole moments of complex compounds of aluminum trihalides with those of gallium shows that in both cases the dipole moments of the complex compounds are greater than the sum of the moments of the component molecules; the increment for compounds of aluminum ($\Delta\mu$ = 5.3 D) is greater than for compounds of gallium ($\Delta\mu$ = 4.7 D) with analogous addends. This signifies also that the polarity of the coordinate bond, which characterizes the tendency to completion of the outer electron shell in the atoms of the metals investigated, changes in the same direction.

In this connection it appeared of interest to investigate the dipole moments of some complex compounds of thallium trichloride and indium tribromide.

In the present investigation measurements were made of the dipole moments of compounds of thallium trichloride with pyridine, quinoline and dioxane, and of indium tribromide with diethyl ether. In the course of these investigations we synthesized new complex compounds of thallium trichloride with dioxane and of indium tribromide with diethyl ether.

EXPERIMENTAL *

Complex compound of thallium trichloride with dioxane. The compound $TlCl_3 \cdot 2C_4H_8O_2$ was prepared from a solution of thallium trichloride in dioxane by slow evaporation of the dioxane in a vacuum-desiccator. Colorless, hexahedral lamellar crystals came down from the supersaturated solution; their analysis for thallium and chlorine corresponded to the composition of the aforementioned compound. When kept for a long period over sulfuric acid, the compound loses dioxane and changes to a white powder of thallium trichloride, thus demonstrating its poor stability. The complex melts with decomposition in a sealed capillary in the temperature range of 65-75°. The complex is slightly soluble in benzene.

The dipole moments were measured by the method of dilute solutions. The procedure and notation have been reported previously [7]. Measurements were performed at 20°.

In Table 1 are set forth the values of the dielectric constants and specific gravities as well as the magnitudes of the dielectric polarization extrapolated to infinite dilution. The magnitude of the dipole moment of the complex is given in Table 5.

Compound of thallium trichloride with pyridine. This compound was obtained by the method of Meyer [8] — introduction of pyridine into an aqueous solution of thallium trichloride; a white, heavy crystalline precipitate of the complex compound came down and was separated from the solution, washed with anhydrous

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* E. V. Redkina took part in the experimental work.

alcohol and then with dry ether, and recrystallized from a mixture of alcohol and ether. The same compound may be prepared more simply by adding pyridine to an ethereal solution of $TlCl_3$.

TABLE 1

Dielectric constants and polarizations of the complex $TlCl_3 \cdot 2C_4H_8O_2$ in benzene

C_2	d	ε	P_2 (cm³)
0.00	0.8785	2.283	—
0.00021	0.8791	2.289	360
0.00042	0.8797	2.292	358

$P_{2\infty} = 360$ cm³

TABLE 2

Dielectric constants and polarizations of the complex $TlCl_3 \cdot 3C_5H_5N$ in benzene

C_2	d	ε	P_2 (cm³)
0.00	0.8785	2.283	—
0.00013	0.8788	2.286	462
0.00029	0.8792	2.290	465
0.00032	0.8793	2.291	474
0.00049	0.8797	2.295	471
0.00052	0.8798	2.297	500

$P_{2\infty} = 460$ cm³

TABLE 3

Dielectric constants and polarizations of the complex $TlCl_3 \cdot 2C_9H_7N$ in dioxane

C_2	d	ε	P_2 (cm³)
—	1.0336	2.218	—
0.00069	1.0355	2.252	793
0.00171	1.0385	2.303	789
0.00204	1.0395	2.321	801
0.00218	1.0399	2.329	806
0.00232	1.0403	2.335	798
0.00272	1.0419	2.358	805

$P_{2\infty} = 800$ cm³

TABLE 4

Dielectric constants and polarizations of the complex $InBr_3 \cdot (C_2H_5)_2O$ in benzene.

C_2	d	ε	P_2 (cm³)
0.00	0.8785	2.283	—
0.00061	0.8803	2.306	599
0.00075	0.8807	2.311	596
0.00087	0.8810	2.316	605
0.00107	0.8816	2.323	595
0.00114	0.8816	2.326	600
0.00133	0.8823	2.332	590
0.00143	0.8827	2.334	570

$P_{2\infty} = 600$ cm³

TABLE 5

Compound	Solvent	$P_{2\infty}$	P_{E+A}	P_0	$\mu \cdot 10^{18}$	
					Complex	Organic molecule
$TlCl_3 \cdot 2C_4H_8O_2$	Benzene	360	75	285	3.66	0
$TlCl_3 \cdot 3C_5H_5N$	Benzene	457	107	350	4.07	2.08
$TlCl_3 \cdot 2C_9H_7N$	Dioxane	800	119	681	5.68	2.15
$InBr_3 \cdot (C_2H_5)_2O$	Benzene	600	63	537	5.04	1.14

Determination of the thallium and chlorine contents of the compound prepared by the latter method showed that its composition corresponds to the formula $TlCl_3 \cdot 3C_5H_5N$. This compound is poorly soluble in water, slightly soluble in benzene, and readily soluble in alcohol and dioxane.

Measurements of the dielectric constants and the calculated polarizations are set forth in Table 2; the dipole moments are in Table 5.

Compound of thallium trichloride with quinoline. The complex compound $TlCl_3 \cdot 2C_9H_7N$ has been prepared previously [9] by addition of quinoline to a saturated solution of thallium trichloride in anhydrous alcohol. We prepared the compound by adding quinoline to a saturated solution of $TlCl_3$ in dry ether. The voluminous white precipitate of the complex was washed several times with ether and dried in vacuum and then over sulfuric acid. Chlorine and thallium determinations confirmed the composition of the complex.

In a sealed capillary the complex melts at 192°.

The compound $TlCl_3 \cdot 2C_9H_7N$ is insoluble in benzene, carbon bisulfide and carbon tetrachloride. Its solubility in dioxane reaches 2%, and for this reason the dipole moment was determined in dioxane.

Table 3 contains the results of determinations of the dielectric constants and polarizations of the complex $TlCl_3 \cdot 2C_9H_7N$ in dioxane; the dipole moment is given in Table 5.

Compound of indium tribromide with diethyl ether. Indium tribromide forms a compound with the composition $InBr_3 \cdot (C_2H_5)_2O$; the dipole moment was determined in benzene. In Table 4 are set forth the measurements of dielectric constants and specific gravities and the calculated values of dielectric polarization.

In Table 5 are set forth the dipole moments of the complexes studied. For their determination the deformation portion of the polarization of the complexes of thallium trichloride was calculated from the molecular refraction of $TlCl_3$, which we measured in dioxane [7], and from the refraction of the organic compound. For the $InBr_3 \cdot (C_2H_5)_2O$ complex the deformation polarization was calculated from the refraction of the corresponding ions and the refraction of diethyl ether. The atomic polarization was assumed to be 10% of the molecular refraction.

We see from the data of Table 5 that the dipole moments of the complex compounds of thallium trichloride with dioxane, pyridine, quinoline and of indium tribromide with diethyl ether are fairly high. A similar phenomenon was previously observed in a study of complex compounds of boron and aluminum halides, and it is explained by the fact that in the formation of complexes between trihalides of indium and thallium on the one hand, and an organic molecule on the other hand, a new coordinative bond is developed. The latter, being more or less polar (depending upon the chemical character of the atoms between which the pole is formed), causes an increase in the dipole moment on linking of the separate molecules to form a complex.

The dipole moments of the investigated complex compounds were determined, as indicated above, in benzene and dioxane as solvents. In the preceding investigation we showed that thallium trichloride in dioxane and benzene has its own dipole moment. This fact is not in conflict, however, with the conclusions since the compounds studied are considerably more stable than the compounds of $TlCl_3$ with the solvents in which the measurements were made, and the data obtained actually characterize the electrical properties of the complex compounds of thallium trichloride with dioxane, pyridine and quinoline, and not with the solvent. Thus, the compound of $TlCl_3$ with benzene is very unstable and it cannot be isolated in the pure state. By contrast, the compound $TlCl_3 \cdot 2C_9H_7N$, whose dipole moment was measured in benzene, is more stable, and it can be obtained in the crystalline state from aqueous solutions. It does not change when recrystallized from alcohol or ether. The same is true of the compound $TlCl_3 \cdot 2C_4H_8O_2$ which may be isolated by crystallizations from dioxane (the dipole moment was determined in benzene). Dioxane in turn is a weaker complex-former than pyridine, since it does not displace pyridine from the complex $TlCl_3 \cdot 3C_5H_5N$.

It is evident from what has been said that the compounds of thallium trichloride with dioxane, pyridine and quinoline are more stable than the compounds which they might form with the solvents used for the measurements.

In complex compounds of thallium trichloride the thallium exhibits coordination numbers of 4 and 6. Consequently $TlCl_3$ can add on 3 molecules of ammonia or an amine with formation, for example, of the compounds $TlCl_3 \cdot 3NH_3$ [10] and $TlCl_3 \cdot 3C_5H_5N$, or 1 molecule of diethyl ether with formation of the compound $TlCl_3 \cdot (C_2H_5)_2O$ [8]. Apart from the types of compounds named, thallium trichloride forms another type of compound with dioxane and quinoline: $TlCl_3 \cdot 2C_9H_7N$ and $TlCl_3 \cdot 2C_4H_8O_2$ [10].

In this connection it is interesting to compare the dipole moments of thallium trichloride with quinoline and the compound of $TlCl_3$ with pyridine which contain a different number of coordinated molecules of amine. Here it must above all be noted that, in spite of the similarity between the character of the addends in the complexes $TlCl_3 \cdot 3C_5H_5N$ and $TlCl_3 \cdot 2C_9H_7N$ and the small difference between the dipole moments of pyridine (2.08) and quinoline (2.15), the dipole moments of their complex compounds differ considerably (4.07 D and 5.68 D); this is bound up with the difference in composition and, consequently, with the different structure of these compounds.

SUMMARY

1. Complex compounds are obtained from thallium trichloride and dioxane and of indium tribromide with diethyl ether with the compositions $TlCl_3 \cdot 2C_4H_8O_2$ and $InBr_3 \cdot (C_2H_5)_2O$.

2. Determinations are made of the dipole moments of some complex compounds of thallium trichloride and indium tribromide: $TlCl_3 \cdot 2C_4H_8O_2$ (μ = 3.66 D), $TlCl_3 \cdot 3C_5H_5N$ (4.07 D), $TlCl_3 \cdot 2C_9H_7N$ (5.68 D) and $InBr_3 \cdot (C_2H_5)_2O$ (5.04 D).

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FORMATION OF SULFIDES IN THE REACTION OF FERROUS SULFIDE WITH METAL OXIDES

I. REACTION OF FeS WITH Al_2O_3 IN PRESENCE OF CARBON

Zh. L. Vert and M. V. Kamentsev

The formation of aluminum sulfide by the action of FeS on Al_2O_3 in presence of carbon has found practical application in the production of alumina by the Haglund method [1]. The literature, however, contains conflicting statements as to the temperature of start of formation of Al_2S_3 and as to the volatility of the sulfide formed. Siebers [2] obtained an insignificant yield of Al_2S_3 at a temperature of about 1300°. According to Oelsen and Maetz [3] a mixture of alumina, FeS and wood charcoal did not undergo a loss in weight at 1400°. Change of weight was found at 1600° but was only considerable at about 1700°.

From the thermodynamic constants of aluminum sulfide necessary for evaluation of the possibility of occurrence of the reaction

$$Al_2O_3 + 3FeS + 3C = Al_2S_3 + 3Fe + 3CO, \tag{1}$$

only the value of $(\Delta H_{298})_{Al_2S_3} = -121550$ cal/mole [4] is known. A low value of the entropy of Al_2S_3 was obtained by us on the basis of the semiempirical equation of M. Kh. Karapetyants [5], derived for various sulfides, and from Eastman's formula [6].

M. Kh. Karapetyants showed that the change of free energy of the reaction

$$\frac{n}{m}\,Me_T + S_{rhomb} = \frac{1}{m}\,Me_nS_m \tag{2}$$

is in linear dependence on the enthalpy which in terms of $\frac{1}{m}$ mole sulfide has the form:

$$\Delta\Phi^\circ_{298} = 0.990\,\Delta H_{298} + 0.17.$$

The latter allows calculation of ΔS of reaction (2) and calculation of $S_{Al_2S_3}$. According to the Eastman equation the entropies of solids (calculated for 1 g-atom) are given by

$$S = \frac{3}{2}\,R\ln\frac{M}{n} + R\ln\frac{M}{n\cdot d} - \frac{3}{2}\,R\ln T_{fus.} + 12.5,$$

where M is the molecular weight, d is the density, n is the number of atoms in the molecule. ($T_{fus.\ Al_2S_3} = 1373°$ K [7], $d_{Al_2S_3} = 2.40$ [8]).

Both methods gave similar results — respectively 30.61 and 30.65 entropy units. The mean value of $S_{Al_2S_3} = 30.63$ entropy units was taken as a basis.

The heat capacity of aluminum sulfide was calculated by summation of the atomic heat capacities, and the heat of fusion was assumed to be 7.3 kcal/mole. The thermodynamic constants of all the remaining components of reaction (1), likewise the heats and the temperatures of the phase transformations, were taken from the handbook of Kubaschewsky and Evans [9].

The values of the change of free energy of reaction (1), calculated by the method of Temkin and Schwartzmann, are set forth in Table 1. According to the calculation the formation of Al_2S_3 commences at about 2120° K (1850° C). The values there given for $\Delta\Phi$ for the reaction

$$Al_2O_3 + 3FeS = Al_2S_3 + 3FeO \qquad (3)$$

show, however, that the exchange reaction does not go in absence of carbon.

TABLE 1

Change of free energy with temperature

Reaction	Change of free energy ($\Delta\Phi$)						
	1400°	1600°	1800°	1900°	2000°	2100°	2200°
(1)	84460	58550	41070	28140	15130	2210	−10880
(3)	154130	154740	–	154080	–	152890	–

The calculated temperature of reaction (1) is considerably higher than the experimental values given in the text.

EXPERIMENTAL

The processes of interaction of oxides of metals with sulfides were investigated by the quenching method. Mixtures for the experiments were made up from FeS (reactive), alumina and petroleum coke. Their chemical compositions are set forth in Table 2. The components of the charge were pulverized, screened through a No. 0125 sieve and thoroughly mixed.

TABLE 2

Chemical composition of starting substances (in weight %)

Component	Al_2O_3	FeS	C	Fe	FeO	Fe_2O_3	CaO	SiO_2	Volatiles, moisture	Other impurities	Σ
Alumina	97.73	–	–	–	–	0.16	0.10	0.22	–	1.71	99.92
Ferrous sulfide	0.22	83.33	–	8.15	7.76	–	–	0.47	0.07	–	100.03
Coke	0.13	–	93.50	–	–	0.05	0.04	0.39	5.90	–	100.01

The reaction vessels were graphite crucibles with covers. Experiments were run in a Tammann furnace in the temperature range of 1100-2000°. The tube of the furnace was arranged horizontally; its far end was tightly closed with an asbestos stopper, and the crucible was placed in the middle of the hot zone between two protective carbon sheets (Fig. 1). The front sheet, as also the graphite stopper, which closed the free end of the tube, had a small hole for escape of gases. When the temperature was measured, the front stopper was removed and the thread of the optical pyrometer focused through the opening of the sheet on to the wall of the crucible. Fluctuations of temperature from the mean during an experiment did not exceed 15°.

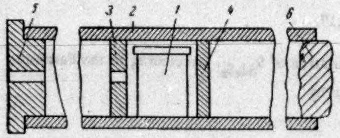

Fig. 1. Arrangement of crucible in tube of Tammann furnace.
1) crucible, 2) tube of furnace, 3) front protective sheet, 4) rear protective sheet, 5) graphite stopper, 6) asbest plug.

After holding for an hour under the specified conditions, the crucible was pushed into the cold zone where it cooled in an atmosphere of carbon monoxide. The reaction product was weighed, pulverized and analyzed.

A complete analysis of the products of reaction was not usually carried out. Since the purpose of the work was the study of the interaction of ferrous sulfide with oxides, determinations were made afresh of the sulfide formed, usually easily decomposable, and of the unreacted FeS.

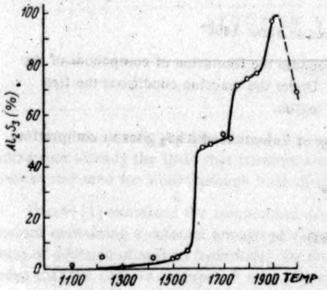

Fig. 2. Yield of Al_2S_3 as a function of temperature.

For determination of the Al_2S_3 content a weighed sample of the clinker (0.08-0.20 g) was decomposed with 5% H_3BO_3 solution in a hydrogen atmosphere [10, 11]. By this procedure the FeS is decomposed to a lesser extent than in decompositon with $MgCl_2$ solution [10] or with water in a CO_2 atmosphere [12].

The H_3BO_3 solution was prepared immediately prior to the analysis and boiled a short period for removal of dissolved oxygen. Decomposition was performed for about 1½ hours with periodic heating of the flask to the boil. The evolved H_2S was absorbed by 0.1 N iodine solution, the excess of which at the end of the decomposition was back-titrated with 0.1 N $Na_2S_2O_3$. For determination of the total content of sulfide sulfur, a weighed sample of the reaction product (0.17-0.10 g) was treated with HCl (1: 3) in presence of 15 ml 1% $SnCl_2$ solution; 40-45 minutes sufficed here for complete decomposition of the Al_2O_3 and FeS.

The composition of the charge for experiments on the interaction of FeS and Al_2O_3 in presence of carbon was calculated from Equation (1) with a slight excess of petroleum coke; it comprised 10 g Al_2O_3, 31.1 g FeS and 4 g C. Allowing for impurities, the starting material contained the main components in the molar ratio: $[Al_2O_3]:[FeS]:[C] = 1:3:3.2$. A sample of 2.5-3 g was taken for an experiment.

The iron formed in the reaction and the excess FeS agglomerated to a bead.

Results of experiments are plotted in Fig. 2 which shows that the sulfide which is decomposed by the boric acid first appears in the charge at about 1400-1500°, and its content rises sharply with further rise of temperature. In the 1600-1730° range the yield of Al_2S_3 (approx. 50% of the theoretical) remains nearly constant, indicating formation of a stable compound. The equimolar ratio of Al_2O_3 to Al_2S_3 in the reaction products indicates that the compound formed is either $Al_2O_3 \cdot Al_2S_3 \cdot FeS$ or, more probably, $Al_2O_3 \cdot Al_2S_3$ — a compound whose existence has been mentioned by a number of authors. Thus, Siebers [2] regards the formation of $Al_2O_3 \cdot Al_2S_3$ as possible on the basis of a study of the fusion diagram of the system $Al_2O_3-Al_2S_3$. N. E. Filonenko and I. V. Lavrov [13] studied the same system and observed the separation from the melt, apart from corundum, of a mineral distinguished by high light refraction and double refraction (n_e 2.07, n_0 1.97). This mineral crystallizes in the hexagonal system and the authors suggest that it is $Al_2O_3 \cdot Al_2S_3$.

Above 1730° the content of sulfide again rises and a fresh plateau is observed in the 1750-1850° region. Judging by the yield (approx. 75% Al_2S_3) the newly formed compound corresponds to $Al_2S_3 \cdot FeS$ (the ratio of Al_2S_3 to FeS in the product is nearly unity).

Formation of $Al_2S_3 \cdot FeS$ was observed by Ditz in an investigation of the reaction between aluminum and ferrous sulfide [14]. The existence of this compound has been confirmed by later studies [15, 16].

Further rise of temperature leads to an increase of the Al_2S_3 yield to 96%; at the same time, however, some of the sulfide sulfur is lost (approx. 2%) and at 200° the losses are so high that the amount of Al_2S_3 falls to 70%. Evidently such a high temperature promotes both the vaporization of Al_2S_3 and FeS and, possibly, the dissociation of Al_2S_3 to AlS and elemental sulfur.

This insignificant yield of decomposable sulfides at a temperature below 1400° is bound up with unavoidable experimental errors as well as with slight decomposition of FeS in boric acid solution.

Heating of a mixture of Al_2O_3, FeS and carbon to above 1400° leads to formation of aluminum oxysulfide

$Al_2O_3 \cdot Al_2S_3$. Like Al_2S_3, the oxysulfide is easily decomposed by water and H_3BO_3 solution with evolution of hydrogen sulfide. Formation of $Al_2O_3 \cdot Al_2S_3$ and of $Al_2S_3 \cdot FeS$ proceeds at a lower temperature than the formation of Al_2S_3. This fact also accounts for the deviation of the calculated temperature of reaction (1) from the experimental values characterizing the appearance in the reaction mixture of decomposable sulfides.

The temperature at which Al_2S_3 is directly formed (1850-1900°) agrees with our calculations. In this interval the formation of sulfide according to reaction (1) goes to completion.

SUMMARY

1. Reaction of FeS with Al_2O_3 in presence of carbon commences at about 1400°

2. The appearance of free Al_2S_3 in the products of reaction precedes the formation of compounds of the reaction components with one another: $Al_2O_3 \cdot Al_2S_3$ and $Al_2S_3 \cdot FeS$. Under the reaction conditions the first of these is stable up to 1700°; the second is stable in the 1730-1850° region.

3. In agreement with thermodynamic calculations the reaction of formation of Al_2S_3 goes to completion at above 1850°.

4. Evaporation or decomposition of Al_2S_3 starts at above 1900°.

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STUDY OF VANADYL TARTRATE COMPLEXES

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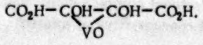
Complex vanadyl compounds and in particular tartrate complexes have not hitherto been adequately studied, but already the little that is known about them (deep color, stability in solutions at high pH, etc.) points to the need for more thorough study of these compounds for their practical utilization.

Ducret [1] examined the composition of a vanadyl tartrate complex compound. He measured the pH of solutions containing a constant amount of vanadyl perchlorate and a variable content of sodium tartrate in the course of addition of sodium hydroxide. On the basis of the plots of pH versus volume of alkali, Ducret concluded that the complex compound contains one vanadyl ion per tartrate ion, and he assigned to it the structure:



$$CO_2H-\underset{\diagdown\,VO\,\diagup}{COH-COH}-CO_2H.$$

Ducret drew attention to the stability of this complex in presence of hydroxyl ions: its decomposition and transition to hypovanadate take place at pH > 12.

It is impossible, however, to fully accept Ducret's conclusions because he studied the complex compound in question only by following the change of pH of the solution, whereas the occurrence of a deep color in this compound points to the expediency of the spectrophotometric method. As will be shown below, however, the spectrophotometric method alone does not give a complete picture of the complex formation, and only by resorting to other methods can one obtain clearer ideas about the vanadyl tartrate complexes.

The polarographic method [2] previously confirmed the formation in solutions of a vanadyl tartrate complex possessing relatively high stability; it suffices to mention that in presence of a considerable excess of Seignette salt the polarographic wave of the vanadyl ion completely disappears. An attempt to determine the composition of the complex ions by the polarographic method [3] was unsuccessful due to the irreversibility of the process of reduction of the vanadyl ion at the dropping mercury electrode.

The present investigation was based upon physico-chemical analysis. Study of the systems specified below was conducted by the method of continuous changes. A particular property was observed (optical density, electrical conductivity, etc.) in solutions containing varying concentrations of vanadyl sulfate and tartaric acid (or its salts) with constant total volume and concentration of solution; corrections were introduced for the same properties of the starting substances, and composition/property graphs were plotted. As we know, the method of continuous changes permits evaluation of the composition of a complex ion or, more precisely, of the stoichiometric ratio of the components forming it.

The following systems were studied: $VOSO_4-KNaC_4H_4O_6$[*]$-H_2O$, $VOSO_4-NaHC_4H_4O_6-H_2O$, $VOSO_4-H_2C_4H_4O_6-H_2O$.

A study was also made of such properties of the solutions as optical density (D), electrical conductivity (w) and pH. In addition, electrolysis was used to solve the problem of the sign of the charge of the ions.

Spectrophotometric investigations were carried out with a vertical FM photometer (Pulfrich type). In separate experiments it was found that the maximum optical density both in solutions of vanadyl sulfate and in solutions of its tartrate complex is observed when using a red (S72) and a yellow (S57) light filter. Electrical conductivity was measured on a normal Kohlrausch bridge with a tube generator of sonic-frequency oscillations. The pH of the solutions was measured with a glass electrode with the help of a LU-2 amplifier and a PPTV-1 potentiometer. All measurements were made on one and the same portion of solution.

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[*] The symbol Tart is subsequently used to denote $C_4H_4O_6$.

Vanadyl sulfate ($VOSO_4 \cdot 3H_2O$) prepared in the laboratory was used; its concentration in solution was determined by titration with a divalent iron salt using phenylanthranilic acid as indicator. The tartaric acid and Seignette salt were chemically pure grades. A solution of sodium acid tartrate was prepared by mixing solutions of tartaric acid and sodium hydroxide.

All experiments were conducted at room temperature.

I. System $VOSO_4 - NaKC_4H_4O_6 - H_2O$

1. The optical density of solutions with a total concentration of 0.1, 0.05 and 0.01 m was investigated. In one cell was a mixture of solutions of vanadyl sulfate and Seignette salt; in the mixture in the other cell the Seignette salt was replaced by an equal volume of water. This enabled the immediate determination of the optical density of the complex formed, $\overline{D}$, from the relation $\overline{D} = D_n - D_1$, where D_n and D_1 are respectively the optical densities of the mixture of solutions of both substances and of the pure solution of the vanadyl salt. Results of measurements are plotted in Fig. 1. We see that the maximum optical density of the solution is observed at a ratio of $\frac{[KNaTart]}{[VOSO_4]} = 1$, on the basis of which we can assume the formation of a complex ion with the composition $[VOR]^{2-x}$ (the question of the composition of the addend R will be considered below]. It should be noted that the position of the maximum is the same when using both filtrates; this indicates [4] the presence in solution under the given conditions of only one colored complex compound. The graph also reveals a regular fall of the absolute value of D with falling total concentration of solution.

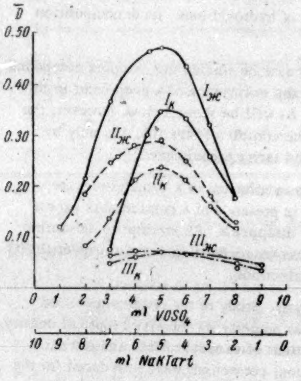

Fig. 1. Change of optical density (D) with changing composition of solution of the system $VOSO_4 - NaKC_4H_4O_6 - H_2O$.
1) 0.1 $\underline{m}$, II) 0.05 $\underline{m}$, III) 0.01 $\underline{m}$. Subscripts $\underline{k}$ and Ж denote the color of the light filter (red, yellow).

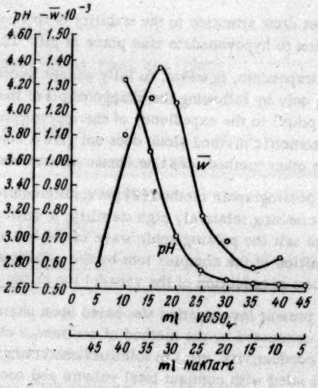

Fig. 2. Change of electrical conductivity ($\overline{w}$) and pH with change of composition of an 0.01 $\underline{m}$ solution of the system $VOSO_4 - NaKC_4H_4O_6 - H_2O$.

2. Measurements were made of the electrical conductivity of pure solutions of vanadyl sulfate (w_2) and Seignette salt (w_3) and their mixtures (w_1). The electrical conductivity corresponding to a solution of the prepared complex (w) was calculated from the formula: $\overline{w} = w_1 - (w_2 + w_3)$.

Results of measurements carried out on 0.01 and 0.05 m solutions (Figs. 2 and 3) indicate the existence of a pronounced maximum $\underline{w}$ at a ratio of $\frac{[NaKTart]}{[VOSO_4]} = 2$. This fact enables us to suspect the existence of a second complex ion with the composition $[VOR_2]^{2-2x}$, whose formation is accompanied by an extremely sharp fall in the total electrical conductivity.

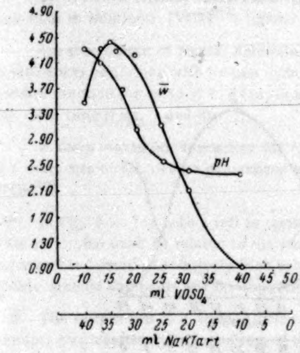

Fig. 3. Change of electrical conductivity ($\bar{w}$) and pH with change of composition of an 0.01 m solution of the system $VOSO_4-NaKC_4H_4O_6-H_2O$.

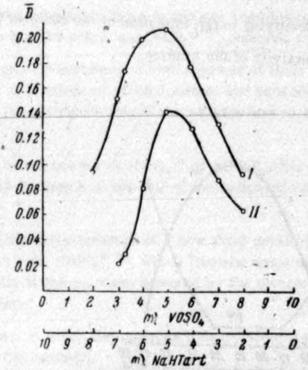

Fig. 4. Change of optical density ($\bar{D}$) with change of composition of 0.05 m solution of the system $VOSO_4-NaHC_4H_4O_6-H_2O$.
I) Yellow light filter, II) red light filter.

3. Simultaneous measurement (during electrical conductivity measurements) of the pH (Figs. 2 and 3) gave results that showed a sharp fall of pH in solutions of both concentrations when the ratio $\frac{[NaKTart]}{[VOSO_4]}$ was close to 2; also, starting from a ratio of unity the magnitude of the pH changes to an insignificant extent (this is more clearly expressed in the 0.05 m solution). This, on the one hand, provides indirect confirmation of the previously surmised formation of two complex ions, and, on the other hand, gives us, for the first time, an indication of the pH regions in which these ions exist.

On comparing the results of a study of the system $VOSO_4-NaKC_4H_4O_6-H_2O$ carried out by all three methods, we can infer the existence of vanadyl ditartrate complexes: $[VOR]^{2-X}$ possessing an intense violet color which is formed at pH < 3 and whose formation is not associated with any appreciable change of electrical conductivity of the solution; the other complex ion, $[VOR_2]^{2-2X}$, exists at pH > 3; during its formation the electrical conductivity of the solution changes markedly, and in these experiments it was impossible to detect by the optical method what could have occurred, due either to the absence of a characteristic color or to a low concentration under the given conditions.

II. System $VOSO_4-NaHC_4H_4O_6-H_2O$

1. Measurements were made of the optical density of solutions with a total concentration of 0.05 m. The results (Fig. 4) confirm the existence of a complex ion with the composition $[VOR]^{2-X}$.

2. Investigation of the electrical conductivity of 0.05 m solutions revealed that it only changed monotonically without any maximum. It should be noted that with rising pH of the solution up to 4.3 by addition of alkali, i.e. by transformation of a part of the acid tartrate into neutral tartrate, there was a complete repetition of the changes observed in the study of the preceding system. This confirms the conclusion that the complex ion $[VOR_2]^{2-2X}$ is formed at higher pH values than the $[VOR]^{2-X}$ ion.

III. System $VOSO_4-H_2C_4H_4O_6-H_2O$

1. In the spectrophotometric investigation of this system in 0.1, 0.005 and 0.001 m solutions it was established that their original color changed to an insignificant extent and that conspicuous maxima were absent from the composition/property curves. This may be due to the formation at low values of pH of only insignificant

amounts of complex ions of $[VOR]^{2-x}$ with little influence upon the color of the vanadyl salt solution.

2. In a study of the system by the conductometric method in 0.05 and 0.01 m solutions the data plotted in Figs. 5 and 6 were obtained; these show that the $\bar{w}$-composition curves contain definite maxima at a ratio of $\frac{[H_2Tart]}{[VOSO_4]} = 1$, testifying to the formation of the complex $[VOR]^{2-x}$ ions which is accompanied by a rise in the electrical conductivity of the solution.

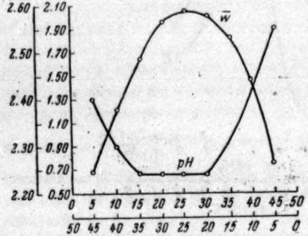

Fig. 5. Change of electrical conductivity ($\bar{w}$) and of pH of 0.01 m solution of the system $VOSO_4-$ $-H_2C_4H_4O_6-H_2O$.

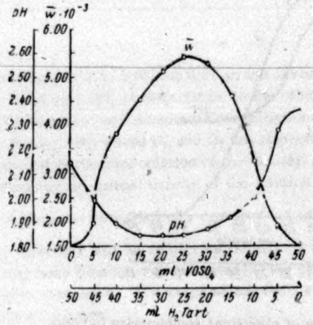

Fig. 6. Change of electrical conductivity ($\bar{w}$) and of pH of 0.05 m solution of the system $VOSO_4-$ $-H_2C_4H_4O_6-H_2O$.

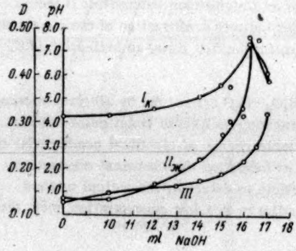

Fig. 7. Change of optical density (D) and of pH in solution of $VOSO_4$ and $NaHC_4H_4O_6$ with addition of NaOH from pH 0.5 to 4.5.
I_k) red light filter, $II_{Ж}$) yellow light filter, III) pH.

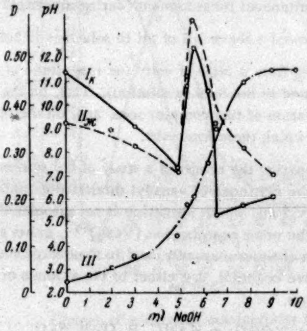

Fig. 8. Change of optical density (D) and of pH in solution of $VOSO_4$ and $NaHC_4H_4O_6$ with addition of NaOH from 2.5 to 11.5.
I_k) red light filter, $II_{Ж}$) yellow light filter, III) pH.

3. The change in the pH was observed at the same time as measurement of the electrical conductivity of the solution; the pH fell markedly, undoubtedly reflecting the process of complex formation, although the absence of a sharp minimum from the pH curve does not permit us to relate this drop to a definite value of the $\frac{[H_2Tart]}{[VOSO_4]}$ ratio. It should be noted in particular that in the course of complex formation the pH value becomes considerably lower than in the original vanadyl sulfate solution (Fig. 6), falling from 2.15 to 1.85 (the cause of this phenomenon will be considered below).

On comparing the data obtained for this system by all three methods, we can confirm the previous conclusion about formation at low values of pH of the $[VOR]^{2-x}$ ion, but only in such minute amounts that they can be detected only by the conductometric method, the latter in this case being more sensitive than the spectrophotometric method.

On the basis of study of all three systems we reached the conclusion that two tartrate complexes of vanadyl ions exist in solutions: $[VOR]^{2-x}$, formed at ph < 3 and with a violet color, and $[VOR_2]^{2-2x}$, observed at pH > 3.

For the purpose of precise determination of the pH limits for formation of both ions and of their color, titration was performed with sodium hydroxide of a mixture of solutions of vanadyl sulfate and acid sodium tartrate taken in the ratio of 1 : 4 (to ensure an excess), and the optical density of the solution was measured at the same time (Figs. 7 and 8).

A sharp maximum appears on the optical desnity/NaOH volume curve of Fig. 7 at pH 2.6, after which there is a sharp rise of pH. These phenomena are explained by the formation of the first of the indicated complexes $[VOR]^{2-x}$,

In Fig. 8 we see both a fall in optical density at pH 2.5 and the presence of a new sharp maximum at pH 6. This maximum must be related to the second of the complex ions, $[VOR_2]^{2-2x}$, which likewise has a deep violet color and is formed at relatively high values of pH; previously it had not been detected by the spectrophotometric method due to its low concentration in an acid medium.

The occurrence of a marked difference in the pH values at which the complex ions mentioned are formed prompts consideration of the problem of the composition of the addends.

For this purpose calculation was made of the relative content of tartaric acid and its anions in solution in dependence upon the pH according to the following formulas:

$$C_{H_2C_4H_4O_6} = \frac{C_{total}}{1 + \frac{K_1}{C_{H^+}} + \frac{K_1 \cdot K_2}{C^2_{H^+}}};$$

$$C_{HC_4H_4O_6^-} = \frac{C_{total}}{1 + \frac{C_{H^+}}{K_1} + \frac{K_2}{C_{H^+}}},$$

$$C_{C_4H_4O_6^{2-}} = \frac{C_{total}}{1 + \frac{C_{H^+}}{K_2} + \frac{C^2_{H^+}}{K_1 \cdot K_2}},$$

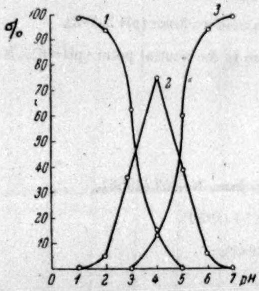

Fig. 9. Relative content of H_2Tart (1), $HTart^-$ (2) and $Tart^{2-}$ (3) in dependence upon the pH of the solution.

where C_{total} = concentration of tartaric acid in moles per liter. These results are shown graphically in Fig. 9 from which it is seen that at pH 2.5-3, of the two anions of tartaric acid, the solution only contains $HC_4H_4O_6^-$; consequently it enters into the composition of the complex ion formed under these conditions, and the latter may be represented by $[VO(HC_4H_4O_6)]^+$.

The second complex ion is formed at a pH of approx. 6; in this case $C_4H_4O_6^{2-}$ anions predominate in the tartaric acid solution (Fig. 9), and consequently the complex can be represented by the formula $[VO(HC_4H_4O_6)]^+$.

The phenomenon of sharp fall of the pH of the solution observed above for the system $VOSO_4-H_2C_4H_4O_6-H_2O$ here finds its explanation. As we see from Figs. 5 and 6, the pH minimum approximately coincides with the maximum of the electrical conductivity of the solution, and accordingly it can be related to the complex formation taking place according to the equation:

$$VOSO_4 + H_2C_4H_4O_6 = [VO(HC_4H_4O_6)]HSO_4.$$

Subsequent dissociation of the compound formed

$$[VO(HC_4H_4O_6)]HSO_4 \longrightarrow [VO(HC_4H_4O_6)]^+ + H^+ + SO_4^{2-}$$

leads to appearance in the solution of H^+ ions and to a corresponding fall of pH.

For solution of the problem of the sign of the charge of the ions and, in turn, for indirect confirmation of the ideas enunciated about their composition, use was made of electrolysis. Into a U-shaped tube fitted with taps was run a mixture of solutions of vanadyl sulfate and complex-former, the latter in excess; the taps were closed and the space above the mixture was filled with faintly acidified distilled water; platinum electrodes were inserted and a constant current of several tens of milliamperes was passed through. After a short period the solution near the cathode became greenish-yellow and a brown turbidity appeared, while lower down the solution acquired a deep, red-violet color. Near the anode was observed a blue color similar to the color of the vanadyl ion. The turbidity must be attributed to formation of vanadyl hydroxide with rise of pH due to secondary processes, while the color of the solution in the cathodic region must have been caused by positively charged complex ions. The blue color observed round the anode could have resulted from movement to the anode of negatively charged ions; the weakness of the color may be due to the low concentration of these ions in an acidic medium.

Electrolysis thus confirms the presence in the solution of two ions with charges of opposite signs.

SUMMARY

1. The formation is demonstrated of two violet-colored tartrate complexes of vanadyl ions.

2. The first has the composition $[VO(HC_4H_4O_6)]^+$ and is formed in an acid medium (pH 2.5-3).

3. The second ion has the formula $[VO(C_4H_4O_6)_2]^{2-}$; it is formed close to the neutral point ($pH \approx 6$). It is distinguished by high stability in a strongly alkaline medium ($pH > 11$).

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INVESTIGATION OF AQUEOUS SOLUTIONS OF DIBASIC ORGANIC ACIDS

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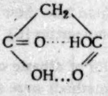
A study of the properties of monobasic organic acids and their aqueous solutions showed that acids in the vapor form and in liquid phases are associated to dimers due to development of an intermolecular hydrogen bond between the carboxyl groups. In aqueous solution with a ratio of 2 moles water to 2 moles acetic acid, a hydrate with a chain structure is formed, a dimer with the composition $2CH_3COOH \cdot 2H_2O$, while with a ratio of 2 moles water per mole of acid a hydrate with the composition $CH_3COOH \cdot 2H_2O$ is formed. Not all the dimers break down on transition to the vapor phase [1].

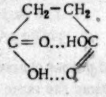
The views concerning the behavior of monobasic organic acids (formic and acetic) were subsequently confirmed by other workers with the help of Raman spectra [2]. Many papers have been published about the study of various organic compounds by the Raman spectrographic method, and on their basis the presence of an intramolecular hydrogen bond has often been established in organic compounds and in high-molecular compounds [3].

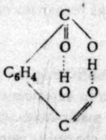
The results of investigations of the characteristics of the behavior of monobasic organic acids also served as a basis for the study of aqueous solutions of dibasic acids. We determined the molecular weight (by the cryoscopic method), the electrical conductivity (specific and molecular), the pH (glass electrode) and the surface tension (σ) in dependence on the concentration and temperature of the solution. Solutions were studied over a wide range of concentrations from extreme dilution to saturation. The water used for preparation of the solutions of dibasic acids had a pH of 6.8.

Figures 1-3 contain curves of the experimental data for malonic, succinic and phthalic acids. Dibasic acids contain two hydrophilic groupings capable of bonding with molecules of water and also of forming dimeric structures. Dibasic acids, however, do not associate and do not add on water. In aqueous solutions of a certain concentration they are monomers; with increasing dilution they dissociate more and more into ions.

The lack of ability to form dimers and to add on water leads to the conclusion that the carboxyl groups of dibasic acids are joined by an intramolecular hydrogen bond, and their molecules have the following configurations:


Malonic acid


Succinic acid


Phthalic acid

It is known that dibasic acids possess two stages of association which are characterized by two dissociation constants; the numerical value of K_1 considerably exceeds the magnitude of K_2. It is also known that dibasic acids form cyclic oxides and have limited solubility. These features of dibasic acids provide some support for the hypothesis of the bridged structure of dibasic acids in aqueous solutions of appropriate concentration.

The surface tension of aqueous solutions of monobasic organic acids shows that these acids exhibit marked surface-active properties which fall off in the region of the aqueous solution in which hydrates containing one and two molecules of water are formed [4]. It appeared of interest to determine the changes in the magnitude of the surface tension in dependence on the composition of the solutions and on the nature of the dibasic organic acids (malonic, succinic and phthalic).

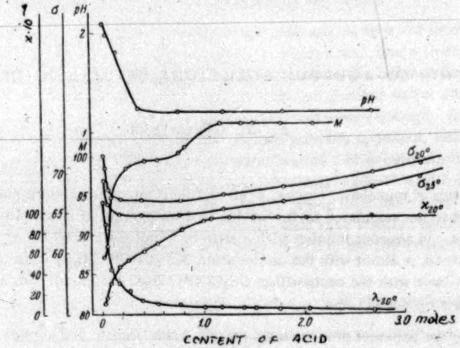


Fig. 1. Physico-chemical properties of solutions of malonic acid.

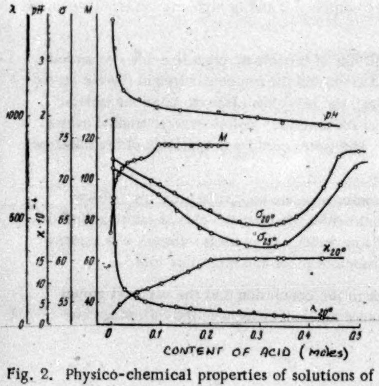


Fig. 2. Physico-chemical properties of solutions of succinic acid.

The surface tension was studied by the method proposed by P. A. Rebinder and now extensively used. As we see from the curves (Figs. 1-3), the surface tension only decreases markedly up to a certain region of concentration of the aqueous solution and thereafter remains constant regardless of the changes of concentration. The surface tension isotherms (20 and 25°) run parallel to the axis of the abscissas. This part of the curve indicates that the surface tension and the capillary activity reach a limiting value [5].

With increase in the number of monomers with bridged structure the surface tension rises and reaches in this region of the solution a value higher than the surface tension of water. The 20° isotherm is similar to the 25° isotherm. Water as a solvent is, as it were, an indifferent medium. The carboxyl groups of the acid lose their hydrophilic and capillary-active properties [6].

With the aim of confirming the results of the investigations characterizing the behavior of dibasic organic acids in aqueous solution in dependence on the concentration, the same physico-chemical methods were applied to a study of the system malic acid-water. It seemed of interest to establish how the molecular structure and properties of malic acid change in dependence on the concentration of the solution when three hydrophilic groupings are involved. It might have been expected that molecules of malic acid in an aqueous solution of appropriate concentration would also be bridged by an intramolecular hydrogen bond formed between the carboxyl groups, similarly to what occurs in solutions of malonic, succinic and phthalic acids.

Capillary-active properties of malic acid are manifested only in the region of dilute solution; the 20 and 25° isotherms of surface tension $(\sigma = f(c))$ are directed downward ; subsequently the curves have horizontal portions. In this region of acid solution (0.02 mole/liter-0.1 mole/liter) σ and Γ attain their limiting values. The 20 and 25° isotherms then again move upward , changing into straight lines that slowly rise with increasing concentration of solution. The surface tension increases gradually and attains values above the surface tension of water at the same temperature: $\sigma_{20°} = 77.7$ dynes/cm and $\sigma_{25°} = 77.0$ dynes/cm. In this region of concentration of solution the carboxyl groups of malic acid do not manifest hydrophilic and capillary-active properties; this may be attributed to bridging of molecules of the acid by an intramolecular hydrogen bond. The solution is nearly saturated in this region.

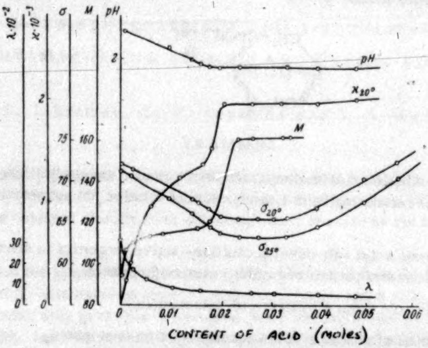


Fig. 3. Physico-chemical properties of solutions of phthalic acid.

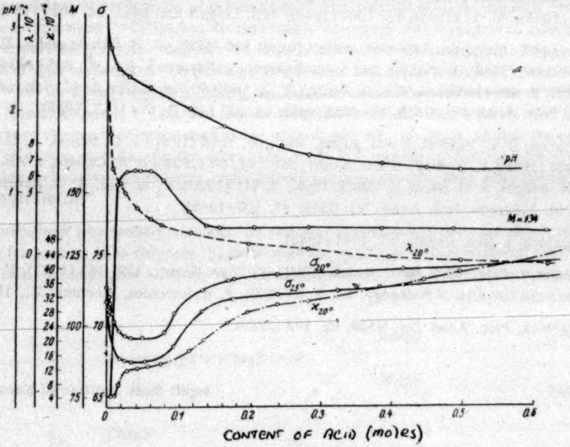
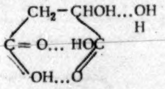


Fig. 4. Physico-chemical properties of solutions of malic acid.

The structure of the molecules of malic acid in aqueous solution and their properties are similar to those of malonic, succinic and phthalic acids. In the region of aqueous solution containing 0.02-0.01 mole acid per liter, the depression of the freezing point of water is only some hundredths of a degree. Such a low depression points to association of the acid molecules. The horizontal portions on the 20 and 25° surface tension curves and the nearly constant value of the electrical conductivity in the same region of solution reflect the corresponding properties of the molecular structure.

There are no grounds for assuming that in an aqueous solution of such low concentration associated molecules of acid can be formed. It is only permissible to assume the existence in this region of solution of heterogeneous association – formation of a water-acid bond, formation of a monohydrate of low stability by means of an intermolecular hydrogen bond at the hydroxyl group with a molecule of water.

The bridged structure of malic acid monomer may be represented in the following form (in analogy with the structures of succinic and other dibasic acids):



SUMMARY

1. It is established that dibasic acids (malonic, succinic, phthalic and malic) lose their hydrophilic and capillary-active properties in a certain region of concentration of solution, do not associate, and do not form hydrates.

2. The investigated dibasic acids only develop capillary-active properties in dilute solutions. Formation of bridged monomers of acid promotes the loss of capillary-active properties.

3. It is shown that malic acid forms a hydrate with low stability.

4. A structure of monomers of dibasic acids in aqueous solution is proposed.

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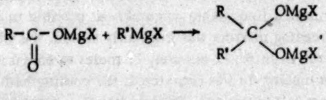
SYNTHESIS OF TRIETHYLCARBINOL AND 3-ETHYLPENTENE-2 FROM ETHYLMAGNESIUM BROMIDE AND CARBON DIOXIDE

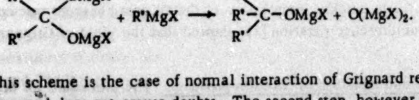
A. L. Liberman, T. V. Lapshina and B. A. Kazansky

3-Ethylpentene-2 is usually prepared from triethylcarbinol, which is obtained by the action of ethylmagnesium bromide on diethyl ketone [1], ethyl propionate [2] or diethyl carbonate [3]. We reasoned, however, that triethylcarbinol could be obtained directly from ethylmagnesium bromide by the action of carbon dioxide under certain conditions.

N. D. Zelinsky described the preparation of benzoic acid in good yield from iodobenzene, magnesium and carbon dioxide [4]. Schroeter [5] attempted to replace iodobenzene in this reaction by the cheaper bromobenzene and found that the latter only gave 7% benzoic acid, but at the same time he obtained triphenylcarbinol (32%) and benzophenone (11%). Later Meyer and Togel [6] showed that benzoic acid is formed in excellent yield also from bromobenzene but at low temperature; at higher temperature they got up to 43% triphenylcarbinol. On acting with carbon dioxide on cyclohexylmagnesium chloride, N. D. Zelinsky observed the formation of tricyclohexylcarbinol. Subsequently he attempted to exploit his observation for preparative purposes and isolated this carbinol, but in extremely low yield [7]. The Bulgarian investigator D. Ivanov [8] made a close study of the conditions of preparation of n-valeric acid from butylmagnesium chloride, and he showed that whereas at low temperature (−20°) carbon dioxide reacts with the Grignard reagent to give 80-85% n-valeric acid, at a higher temperature (36°) the yield of acid falls; at the same time considerable amounts of dibutyl ketone and tributylcarbinol were found. On passing 0.3-0.5 mole CO_2 into a solution of 1 mole n-butylmagnesium chloride at −20° for 2 hours and then boiling the mixture with stirring for 14 hours at 36°, the yield of acid is only 8-9%, that of ketone is 7-11%, and that of carbinol is 45-51%. Here we may note that Schroeter [5] evidently performed the reaction mentioned above without cooling: he points out that the temperature rose during passage of the carbon dioxide. On the other hand, N. D. Zelinsky introduced the carbon dioxide into the solution of cyclohexylmagnesium chloride under intense cooling; this may have been the cause of the low yield of tricyclohexylcarbinol.

In order to understand why tertiary alcohols and ketones are obtained in the cases described above, we must recall that as far back as 1904 Grignard [9] discovered the ability of salts of carbonic acids to react with organomagnesium compounds to give alcoholates of tertiary alcohols. Grignard proposed the following scheme for this reaction:


(1)


(2)

The first step in this scheme is the case of normal interaction of Grignard reagents with substances containing the carbonyl group and does not arouse doubts. The second step, however, appears improbable to us since if the substitution of an OMgX group really takes place, it remains unexplained why substitution of the second such group was not observed with formation of a hydrocarbon containing a quaternary carbon atom.

In our opinion the reaction most probably goes in three steps. It can be expected that the compound $RR'C(OMgX)_2$, being an alcoholate of the unstable glycol $RR'C(OH)_2$, is also unstable and breaks down on heating with formation of a ketone which by reaction with a second molecule of $R'MgX$ gives the alcoholate of the tertiary alcohol. In this manner tertiary alcohols were evidently formed in the previously cited researches. The salts of carbonic acid, formed by the action of CO_2 on Grignard reagent, react further with RMgX to give a glycolate which also gives a ketone, and thereafter the alcoholate of the tertiary alcohol:

$$RCOOMgX + RMgX \longrightarrow R_2C(OMgX)_2, \tag{1}$$

$$R_2C(OMgX)_2 \longrightarrow R-CO-R + MgX_2 + MgO, \tag{2}$$

$$R-CO-R + RMgX \longrightarrow R_3COMgX. \tag{3}$$

The non-decomposed $R_2C(OMgX)_2$ is found in the end products of the reaction in the form of ketone.

Being in need of considerable amounts of 3-ethylpentene-2, we decided to apply the observations set forth above to the development of a convenient and rapid method of preparation of this hydrocarbon. By carrying out 9 syntheses (6 with 2 moles, 1 with 6 moles and 2 with 12 moles ethyl bromide) we satisfied ourselves that triethylcarbinol and 3-ethylpentene-2 can actually be obtained by this route. The yield of pure carbinol was 28% (reckoned on the ethyl bromide); in addition we obtained 10% 3-ethylpentene-2, 6% diethyl ketone and 2% propionic acid. Dehydration of triethylcarbinol gave 26% 3-ethylpentene-2 (reckoned on the original ethyl bromide). Consequently the total yield of 3-ethylpentene-2 was 36%. The possibility of slight improvement in the yield of triethylcarbinol and 3-ethylpentene-2 is not excluded. During the investigation it was established that there is no need to heat the reaction mixture for as long as Ivanov did: if CO_2 absorption is effected at 10-14° the reaction can go to completion fairly quickly. Actually, by working under such conditions even with use of 12 moles ethyl bromide, preparation of the Grignard reagent, absorption of the latter and heating only require 15 hours.

Fairly wide variation of the reaction conditions did not bring about an appreciable increase of yield; in 8 out of the 9 syntheses the yield of the 80-92° fraction (100 mm), containing predominantly triethylcarbinol, was 34-43%.

All the compounds that we prepared were thoroughly purified by various methods; their constants are given below.

EXPERIMENTAL

The Grignard reagent was prepared in a three-necked flask fitted with a powerful stirrer with a mercury seal, a reflux condenser, a thermometer with a long stem reaching to the bottom of the flask, a dropping funnel and an inlet tube for nitrogen. The apparatus was checked for tightness, after which the reflux condenser was connected to a Tishchenko bottle containing sulfuric acid. With this design of apparatus it was easy to detect whether air was sucked into it during cooling. In the flask were put the required amount of magnesium plus an excess of 1-3 g and 100 ml absolute ether for each gram-atom magnesium; the air was then completely driven out by dry nitrogen. Into the flask was then quickly run 5-10 ml ethyl bromide, and the remaining halide was diluted with twice the amount of absolute ether. When the reaction had started (usually after 1-2 minutes), the flask was immersed in a freezing mixture of water, salt and ice, the stirrer was started at a speed ensuring vigorous stirring, and the bromide was run in a fine stream as quickly as possible to avoid aspiration of air through the Tishchenko bottle. If the freezing mixture was frequently stirred, the whole addition could be effected very quickly: 2 moles could be run in in 10-12 minutes, 12 moles in 55-60 minutes; the reaction mixture usually heated up to 50-60°. When running-in was completed, the cooling bath was removed in order that the temperature of the mixture should not fall below 40°. Stirring was then continued for 30-40 minutes. When the temperature had started to fall fairly quickly, preparation of the Grignard reagent was considered complete. In one of the experiments Gilman acidimetric titration [10] showed that the yield of Grignard reagent by this method was about 95%.

Absorption of carbon dioxide and isolation of reaction products. The procedure for bringing carbon dioxide into reaction with the Grignard reagent was not exactly the same in all experiments. However, in all experiments the Grignard reagent was first cooled to 0-5°, the stirrer was then stopped, the nitrogen was quickly purged out of the flask with dry carbon dioxide, and the stirrer was again started at maximum speed; the CO_2 began to be rapidly taken up and the reaction mixture heated up spontaneously. The desired temperature was maintained in the flask with the help of the cooling bath; here occasional stirring of the freezing mixture enabled the time needed for absorption of the carbon dioxide to be reduced. CO_2 was admitted at such a speed that its excess was not discharged through the Tishchenko bottle, and at the same time no air was sucked through this bottle. In Experiments 1, 2 and 3 CO_2 was admitted directly from a cylinder and the amount of absorbed gas was not calculated; in the subsequent experiments the required volume of gas was admitted from a gas-holder. When the absorption of the required amount of CO_2 was ended, the stirrer was stopped, the carbon dioxide displaced by dry nitrogen, and the reaction mixture stirred at the boiling point of ether for complete removal of the Grignard reagent (until the Gilman test [11] was negative). The temperatures of absorption of the CO_2 and the duration of the final stirring are set forth in the table.

Experiment	Taken in reaction			Temperature of absorption of CO_2	Duration (in hours)		Yield of triethylcarbinol fraction (in %)
	C_2H_5Br (in moles)	CO_2			of CO_2 absorption	of final boiling	
		(in moles)	(in moles per mole C_2H_5Br)				
1	2	Without limit	–	42-44°	–	–	36
2	2	Ditto	–	55-60	–	–	30.5
3	2	Ditto	–	59-62	–	–	37.5
4	1.75	0.62	0.35	12-14	2.5	5.5	35.5
5	2	0.66	0.33	5-12	2.5	3 •	35.5
6	2	0.60	0.30	0-15	2.5	10 ••	32
7	6	1.72	0.29	~0	4	10 ••	24.5
8	12	4.00	0.33	0-8	14	2	42.5
9	12	4.00	0.33	10-14	8	3	38.5

• Experiment with substitution of toluene for part of the ether; boiling effect at 70°.

•• Boiling was prolonged in this experiment because due to a small deficiency of CO_2 the residue of organomagnesium compound did not disappear for a long time.

A comparison of the duration of Experiments 8 and 9, which were performed under identical conditions except for the temperature in the flask during absorption of CO_2, shows that in order to carry out the synthesis with maximum rapidity, this temperature must be kept no lower than 10°. As soon as the Gilman test reaction was negative, the reaction mass was cooled and set aside overnight.

In one experiment (5), after CO_2 absorption, the ether was replaced by toluene to raise the temperature of final boiling; this did not, however, have a favorable effect and actually hindered separation of the ketone and olefin, which in this experiment were discarded with the toluene fraction.

The next day the reaction complex was decomposed by transferring the reaction mass (usually solidified) into a mixture of water and ice. The magnesium salts were then dissolved by addition of dilute (3: 1) sulfuric acid, the ether layer was separated, and the aqueous layer thrice extracted with ether. The ether layer plus the combined ethereal extracts were treated twice with 25% sodium hydroxide solution for removal of propionic acid, and then washed with water and dried over potassium carbonate. The alkaline extracts from syntheses 2-9 were combined and from them was isolated 68.5 g (2.3%) propionic acid, b. p. 140.8-141.3° (760 mm), n_D^{20} 1.3870, d_4^{20} 0.9924.

According to the most reliable literature data [12], propionic acid has the constants: b.p. 140.80° (760 mm), n_D^{20} 1.38650, d_4^{20} 0.99336; degree of purity 99.81%.

The ether extracts from each synthesis were, after removal of propionic acid, freed from ether and distilled in vacuum (100 mm) to give two fractions: fraction A with b.p. up to 80° and fraction B with b.p. 80-91°. The latter is the triethylcarbinol fraction; the yields of fraction B in the various syntheses are given in the table. In all were obtained 338.3 g fraction A and 579.8 g fraction B. Distillation of fraction A in a column gave 13 g low-boiling fraction, 271 g fraction boiling at 62.2-92.4° (760 mm) and later subjected to chrom graphic resolution, and a further 13.8 g triethylcarbinol. Thus the yield of fraction B was 593.6 g. On atten ing to distill triethylcarbinol in a column in vacuum (60 mm), dehydration commenced and the distillation had to be stopped; it was nevertheless possible to obtain 85 g of a fraction containing an azeotropic mixture of diethyl ketone and 3-ethylpentene-2, and 36 g pure 3-ethylpentene-2. The fractionation residue of 443.3 g (27.8%) was nearly pure triethylcarbinol [b.p. 67.5-67.6° (40 mm), n_D^{20} 1.4303].

A large portion of the triethylcarbinol was dehydrated for preparation of 3-ethylpentene-2; a small portion was thoroughly purified with the objective of accurately determining its constants.

Purification of triethylcarbinol was effected by −40°.

B.p. 84.7-84.8° (92 mm), freezing point −12.55°, n_F^{20} 1.43534, n_D^{20} 1.43018, n_C^{20} 1.42811, d_4^{20} 0.84511 cryoscopic constant 0.0114 mol. fraction/1° C, degree of purity 99.8% (by the freezing curve method).

The constants of triethylcarbinol reported in the literature deviate fairly widely from one another. Thus the data for refractive index are given as n_D^{22} 1.4266 [13], n_D^{20} 1.4294 [14] and n_D^{20} 1.4330 [14]; the specific gravity is variously reported as d_4^{22} 0.8407 [13] and d_4^{20} 0.842 [14]. The solidifying or melting point of triethylcarbinol is not given in the literature.

It may be claimed that our preparation of triethylcarbinol is the purest of any so far described.

Chromatography of fraction A. Fraction A (270 g), distilled in a column, and the mixture of diethyl ketone and 3-ethylpentene-2 obtained in attempted distillation in a column of triethylcarbinol (85 g), were combined and subjected to chromatography with the objective of separating the diethyl ketone from the 3-ethylpentene-2. Into a column of normal type [15] was put 165-170 g silica gel and 70 g fraction was run in. When the whole had been taken up by the silica gel, 50 ml acetone was run in as resolving liquid; water served as the displacing liquid. After the first 2-3 ml with refractive index higher than that of 3-ethylpentene-2, this hydrocarbon came off in the pure state (n_D^{20} 1.4149, d_4^{20} 0.7212); in all 132 g hydrocarbon was collected (10.3% reckoned on the ethyl bromide). When the refractive index started to fall, the transition fraction was collected prior to the appearance of pure acetone; pure acetone was next collected, followed by a mixture of acetone and diethyl ketone; the transition fraction was subjected to a second resolution by the same method. The mixture of acetone and diethyl ketone was distilled in a column with an efficiency of 35 theoretical plates since very pure diethyl ketone was required for another synthesis. In this way 108.7 g diethyl ketone was obtained (6.4% reckoned on the ethyl bromide). It had the following properties:

B.p. 102.1° (760 mm), freezing point −39.1°, n_F^{20} 1.39721, n_D^{20} 1.39227, n_C^{20} 1.39034, d_4^{20} 0.81430, cryoscopic constant 0.0149 mol. fraction/1° C, degree of purity 99.5%.

The most reliable literature data are those of Dreisbach and Martin [12]: b.p. 101.70° (760 mm), freezing point −39.50°, n_D^{20} 1.39240, d_4^{20} 0.81440, degree of purity 99.6%.

Comparison of the freezing points of the two specimens leads us to think that the American authors slightly overrated the purity of their specimen; judging by the cryoscopic constant found by us, its purity is 99.0%.

Preparation of 3-ethylpentene-2. Triethylcarbinol (428 g) was charged into a column packed with single-spiral glass rings, efficiency about 20 theoretical plates, and distilled in vacuum (113 mm). The hydrocarbon, formed by dehydration, came over at about 40° in the form of an azeotropic mixture with water. In this manner 351.5 g unpurified 3-ethylpentene-2 (97.2% reckoned on the triethylcarbinol) was collected. Together with the amount obtained in the previous attempt to distil triethylcarbinol, this makes a total yield of 387.6 g hydrocarbon by dehydration. The hydrocarbon (387.0 g) was distilled in a copper-packed column with an efficiency of 80 theoretical plates. This fractionation gave 285.7 g 3-ethylpentene-2 with the correct boiling point and 66.8 g rather less pure hydrocarbon; the residue (mixture of 3-ethylpentene-2 and triethylcarbinol) amounted to 30.3 g. Dehydration gave, in all, 352.5 g 3-ethylpentene-2, i.e. a yield of 26.2% reckoned on the ethyl bromide. A total of 484.5 g (36.5%) of this olefin was thus isolated at various stages of the investigation. Pure 3-ethylpentene-2 had the constants:

B.p. 96.2° (760 mm), n_F^{20} 1.42128, n_D^{20} 1.41488, n_C^{20} 1.41238, d_4^{20} 0.72053.

According to the most reliable literature data [16] 3-ethylpentene-2 has the constants: b.p. 96.01° [illegible]m), n_D^{20} 1.4148, d_4^{20} 0.7204.

Al

dioxide

SUMMARY

experim

purge[illegible]. It is shown that reaction of carbon dioxide with ethylmagnesium bromide under certain conditions beg[illegible]s triethylcarbinol from which 3-ethylpentene-2 can be prepared.

2. A preparation of triethylcarbinol purer than the preparations described in the literature has been obtained and its constants determined.

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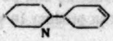
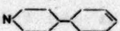
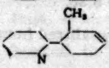
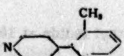
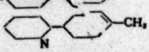
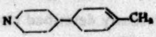
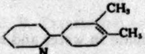
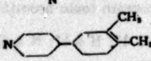
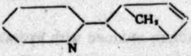
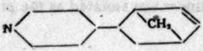
CONJUGATED SYSTEMS

LIX. CONDENSATION OF γ-VINYLPYRIDINE WITH DIENE HYDROCARBONS

A. A. Petrov and V. Lyudvig

Several papers have already been published on the condensation of α-vinylpyridine with diene hydrocarbons [1-4]. One of these [4] is by the present authors. These studies established that α-vinylpyridine resembes acrylonitrile in reactivity. Products of the diene synthesis with participation of α-vinylpyridine — α-cyclohexenylpyridine and its homologs — have been used for preparation of other substituted pyridines, for example arylpyridines.

TABLE 1

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR		Melting point of picrate
				Found	Calculated	
	125°	1.0150	1.5444	49.55	50.67	114°
	140—141	1.0211	1.5472	49.46	50.67	153
	132—133	0.9958	1.5374	54.37	55.29	110—111
	144—145	1.0020	1.5394	54.19	55.29	141
	141—141.5	0.9956	1.5382	54.45	55.29	107—108
	151.5—152	1.0032	1.5420	54.35	55.29	124
	154	0.9937	1.5410	59.22	59.91	101, 106—107
	167—168	0.9984	1.5420	59.05	59.91	143—144
	133—134	1.0621	1.5578	51.95	53.09	142—143
	146—148	1.0665	1.5590	51.84	53.09	140

Only one communication has appeared on the susceptibility to condensation of β-vinylpyridine, and this showed that heating of β-vinylpyridine with butadiene for 40 hours at 125° gave β-cyclohexenylpyridine in a yield of 33%[3].

The condensation of γ-vinylpyridine with diene hydrocarbons has not previously been described.

We investigated the reaction of γ-vinylpyridine with butadiene, piperylene, isoprene, diisopropenyl and cyclopentadiene. In all cases normal products were obtained in a yield of about 50%. These are colorless liquids with a characteristic odor which is pleasanter than that of the isomers of the α-series. In Table 1 are compared the constants of the compounds prepared from α- and γ-vinylpyridines, from which we see that the isomers of the γ-series have higher boiling points, specific gravities and refractive indices. The molecular refractions found for the γ-cyclohexenylpyridines are, as in the case of the α-series, lower than the calculated values.

Crystalline picrates of all the condensation products were prepared. Their melting points are given in Table 1. All the substances, apart from that prepared from cyclopentadiene, were also subjected to dehydrogenation over palladium. The resultant arylpyridines were isolated in the form of picrates.

Several other reactions of these compounds were studied, starting from γ-cyclohexenylpyridine.

Oxidation of γ-cyclohexenylpyridine with potassium permanganate gave isonicotinic acid. Treatment of its chloroform solution with bromine gave a crystalline dibromide. Under similar conditions α-cyclohexenylpyridine gives the hydrobromide of an unsaturated monobromo compound [4]. Consequently the bromine atoms in the dibromide of γ-cyclohexenylpyridine are more stable. Heating of γ-cyclohexenylpyridine with methyl iodide gave the crystalline methoiodide.

EXPERIMENTAL

γ-Vinylpyridine was prepared from γ-hydroxyethylpyridine by distillation with a small quantity of KOH. γ-Hydroxyethylpyridine was prepared by prolonged boiling at normal pressure of a mixture of β- and γ-picolines with formaldehyde. The substance taken for condensation had b.p. 67-70° (18 mm), n_D^{18} 1.5478.

According to the literature γ-vinylpyridine has b.p. 64-67° (15-16 mm), n_D^{20} 1.5452 [5].

Condensation of γ-vinylpyridine with butadiene. 10 g γ-vinylpyridine, 12 ml butadiene, and 50 ml xylene were heated in sealed glass tubes at 170° for 10 hours. Fractionation of the reaction product in vacuum gave 7 g (44%) γ-cyclohexene-3-yl-pyridine.

Found %: C 83.32; H 8.36; N 8.93. $C_{11}H_{13}N$. Calculated %: C 82.93; H 8.23; N 8.80.

The picrate of the compound was prepared under the usual conditions. It was recrystallized from water.

Found %: N 14.51. $C_{17}H_{16}O_7N_4$. Calculated %: N 14.43.

The methiodide was prepared by heating the compound with a small excess of methyl iodide at 100° in a sealed tube for 2 hours; m.p. 85° (from alcohol).

Found %: N 4.58. $C_{12}H_{16}NI$. Calculated %: N 4.65.

Oxidation of the condensation product with potassium permanganate under previously described conditions [4] gave isonicotinic acid. It was identified by a mixed melting test.

Bromination of the condensation product in chloroform gave a dibromide insoluble in water and soluble in organic liquids with m.p. 80.5-81° (from isopropyl alcohol + water). It does not contain ionic bromine.

Found %: C 41.52; H 4.36; N 4.65; Br 50.45. $C_{11}H_{13}NBr_2$. Calculated %: C 41.47; H 4.11; N 4.39; Br 50.09.

0.2 g of γ-cyclohexenylpyridine, 0.45 g maleic anhydride, 0.3 g palladium reduced with hydrazine and 10 ml H_2O were refluxed 5 hours. The reaction product – γ-phenylpyridine – was isolated as the picrate with m.p. 196-197° (from alcohol).

According to the literature the picrate of γ-phenylpyridine has m.p. 197.5° [6].

Found %: N 14.85. $C_{17}H_{12}O_7N_4$. Calculated %: N 14.58.

The experimental data for the condensation of γ-vinylpyridine with other diene hydrocarbons are given in Table 2.

TABLE 2

Product of condensation	Yield (in %)	Found (%)			Calculated (%)			Nitrogen in picrate (in %)	
		C	H	N	C	H	N	found	calculated
With piperylene	58	83.40	9.00	7.95	83.19	8.73	8.08	13.90	13.93
With isoprene	56	83.06	8.81	8.28	83.19	8.73	8.08	14.15	13.93
With diisopropenyl	50	83.48	9.21	7.62	83.35	9.15	7.48	13.46	13.46
With cyclopentadiene	45	84.02	7.67	8.11	84.17	7.65	8.18	14.16	14.00

The picrate of γ-(3,4-dimethylphenyl)-pyridine (prepared from diisopropenyl) melted at 184-186°.

Found %: N 13.96. $C_{18}H_{14}O_7N_4$. Calculated %: N 14.07.

SUMMARY

1. The condensation was investigated of γ-vinylpyridine with butadiene, piperylene, isoprene, diisopropenyl and cyclopentadiene; in all cases the normal products of homocyclization were formed.

2. Crystalline picrates were prepared from all the condensation products.

3. Reactions of γ-cyclohexenylpyridine were used to illustrate the behavior of the condensation products toward oxidizing agents, dehydrogenation catalysis, bromine in chloroform, and methyl iodide. Oxidation of γ-cyclohexenylpyridine gave isonicotinic acid. Dehydrogenation over palladium gave γ-phenylpyridine. Bromine gave the normal dibromide. Heating with methyl iodide led to formation of a crystalline methoiodide.

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* T. p. = C. B. Translation pagination.

THE SYNTHESIS OF NEROL AND GERANIOL

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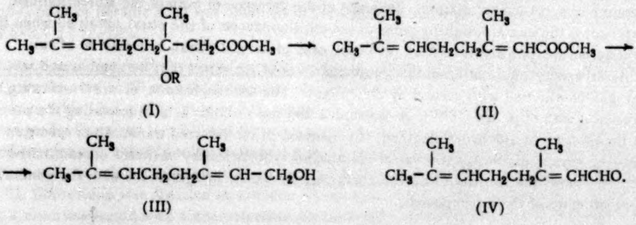
In the complete synthesis of the terpene alcohols nerol and geraniol (III) described by us [1], the intermediate stage is the dehydration of the ester of β-hydroxy-α,β-dihydrogeranic acid (I) (R = H):



$$CH_3-\overset{CH_3}{C}=CHCH_2CH_2\underset{OR}{\overset{CH_3}{C}}-CH_2COOCH_3 \longrightarrow CH_3-\overset{CH_3}{C}=CHCH_2CH_2\overset{CH_3}{C}=CHCOOCH_3 \longrightarrow$$

(I) (II)

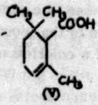
$$\longrightarrow CH_3-\overset{CH_3}{C}=CHCH_2CH_2\overset{CH_3}{C}=CH-CH_2OH \qquad CH_3-\overset{CH_3}{C}=CHCH_2CH_2\overset{CH_3}{C}=CHCHO.$$

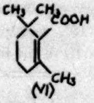
(III) (IV)

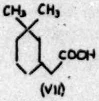
It is of interest to determine the structure of the products of dehydration, likewise the ratio of the stereoisomeric esters of geranic acid (II) formed in this process and of the alcohols (III) obtained by their reduction with lithium aluminum hydride.

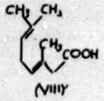
Condensation of methylheptenone with methyl bromoacetate [2] proceeds very vigorously under the action of activated zinc, and distillation of the reaction product gives the hydroxy ester (I, R = H) in a yield of 75-80%.

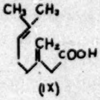
It is known that removal of water with the help of phosphorus tribromide in presence of pyridine gives a mixture of isomeric unsaturated acids [3]. On the other hand, the compound obtained by thermal decomposition of the acetyl derivative of the hydroxy ester (I, R = $COCH_3$) and subsequent saponification more closely resembles the acid obtained by oxidation of citral (IV) [3]. The difference between the acids obtained by different methods of dehydration is manifested most conspicuously when they are cyclized under the action of sulfuric acid solution in concentrated formic acid. Among the products of this reaction are α- and β-cyclogeranic acids (V, VI) and allocyclogeranic acid (VII) which has properties markedly different from those of V and VI. Allocyclogeranic acid (VII) is the predominating substance formed on cyclization of the product of dehydration of the hydroxy ester with phosphorus tribromide. It has been assumed [3, 4] that in the process of dehydration, apart from esters of geranic acid (II), its isomeric β,γ-unsaturated esters (VIII, IX) can be formed, cyclization of which is also the cause of formation of allocyclogeranic acid (VII):


(V)


(VI)


(VII)


(VIII)

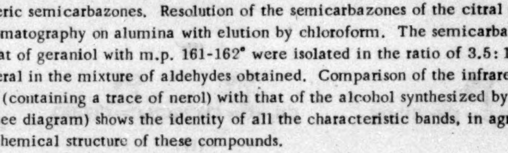

(IX)

In this investigation we realized the cleavage of water from the esters of β-hydroxy-α,β-dihydrogeranic acid by two methods: thermal decomposition of the acetate of the methyl ester (I, R = $COCH_3$) and substitutive halogenation and removal of hydrogen halide with phosphorus oxychloride in presence of pyridine. The esters obtained in both cases were reduced with lithium aluminum hydride to aliphatic alcohols under conditions which left the double bond in the α,β-position intact [5]. A mixture of carbinols was isolated with the very pleasant odor characteristic of nerol and geraniol.

The alcohols were subjected to oxidation with activated manganese dioxide in ligroine [6]. As we know, this reaction is very specific since under the chosen conditions only α,β-unsaturated alcohols are oxidized.

In both cases the mixtures of aliphatic terpene alcohols synthesized by us are, just like natural geraniol, smoothly oxidized to citral, from which the crystalline semicarbazone was obtained in all cases. We observed oxidation of the original alcohol (disappearance of the positive reaction in the Tserevitinov test for the hydroxyl group) independently of which the dehydrating agent was employed for preparation of the esters of geranic acid. Consequently, both methods lead predominantly to the esters of the α,β-unsaturated geranic acid.

When the mixture of alcohols obtained by reduction with lithium aluminum hydride of the products of thermal decomposition of the acetyl derivative (I, R = $COCH_3$) is treated with anhydrous calcium chloride (with geraniol solid addition products are formed), not less than 85% of the original alcohol remains uncombined; this points to preponderance of nerol in the mixture. Evidence of the presence of both of the stereoisomeric forms in the original alcohol is the unsharp melting point of the semicarbazone of the citral obtained when the alcohol is oxidized. Numerous recrystallizations lead, as in the case of natural citral, to isolation of two individual isomeric semicarbazones. Resolution of the semicarbazones of the citral that we synthesized was realized by chromatography on alumina with elution by chloroform. The semicarbazone of neral with m.p. 169-170° and that of geraniol with m.p. 161-162° were isolated in the ratio of 3.5: 1, demonstrating the predominance of neral in the mixture of aldehydes obtained. Comparison of the infrared transmission spectrum of natural geraniol (containing a trace of nerol) with that of the alcohol synthesized by us (nerol contaminated with geraniol) (see diagram) shows the identity of all the characteristic bands, in agreement with the general features of the chemical structure of these compounds.



EXPERIMENTAL

Methyl ester of β-hydroxy-α,β-dihydrogeranic acid (I, R = H)

A solution of 12.7 g methylheptenone and 17.6 g methyl bromoacetate in 80 ml anhydrous benzene was added gradually to 9.0 g activated zinc catalyst kept under a layer of 20 ml anhydrous benzene heated to the boil. In 2-3 minutes after the start of the addition, an exothermic reaction commenced, due to which the boiling continued. After all the solution had been added, heating was continued for 20-30 minutes; the mass was then cooled and 50 ml 10% acetic acid solution was added. The benzene layer was separated, washed with saturated sodium bicarbonate solution and dried with sodium sulfate. After driving off the benzene, the residue was distilled in vacuum (3 mm) to give two fractions: b.p. 55-85° and 108-115°. Redistillation of the second fraction gave the methyl ester of β-hydroxy-α,β-dihydrogeranic acid (I, R = H) in the form of a colorless mobile liquid. Yield 15-15.6 g (75-78%).

B.p. 108-110° (3 mm), d_4^{22} 0.9744, n_D^{22} 1.4568, MR_D 55.88. $C_{11}H_{21}O_3\vDash$. Calc. 55.71.

Found %: active hydrogen 0.494. Calculated %: active hydrogen 0.500.

Methyl ester of β-acetoxy-α,β-dihydrogeranic acid (I, R = $COCH_3$)

A solution of 15.2 g of the ester of β-hydroxy-α,β-dihydrogeranic acid (I, R = H) in 278 g of acetic anhydride was heated at the boiling point for 6 hours. After cooling, the reaction mass was poured into 250 ml of water and extracted with ether. The ethereal solution was washed with saturated sodium bicarbonate solution and dried with sodium sulfate. After driving off the ether, the residue was vacuum distilled and the methyl ester of β-acetoxy-α,β-dihydrogeranic acid was obtained. Yield 15.8-16.2 g (86-88%).

B.p. 118-120° (6 mm), d_4^{22} 0.9938, n_D^{22} 1.4508, MR_D 65.36. $C_{12}H_{22}O_4\overline{F}$. Calc. 64.96.

Reaction for the hydroxyl group (Tserevitinov) negative.

Methyl ester of geranic acid (II)

A mixture of 16.0 g of the methyl ester of the acetate of β-hydroxy-α,β-dihydrogeranic acid (I, R = = $COCH_3$) and 0.1 g anhydrous potassium acetate was slowly heated at a rate such that the vapor temperature did not exceed 185°. 4 ml acetic acid was distilled off, after which the heating was stopped and the residue was cooled and dissolved in ether. The ethereal solution was washed with water and then with saturated sodium bicarbonate solution and dried with sodium sulfate. The ether was driven off, and after distillation in vacuum the methyl ester of geranic acid was obtained in the form of a colorless mobile liquid. B.p. 93-95° (5 mm). Yield 8.5-8.7 g (70-72%).

Reduction of the methyl ester of geranic acid with lithium aluminum hydride. A solution of 8.5 g methyl ester of geranic acid in 20 ml anhydrous ether was added dropwise with stirring to a suspension of lithium aluminum hydride (2.3 g of hydride of 90% purity in 100 ml ether) at a temperature of −50 to −60°. The temperature was gradually raised to −30° and the mass stirred for 1 hour, after which 10 ml ethyl acetate and 20 ml saturated ammonium chloride solution were run in. The ether layer was separated, the aqueous layer extracted with ether, and the ether extracts washed with water and dried with sodium sulfate. After the ether had been driven off, the residue was distilled in vacuum. A mixture of the alcohols nerol and geraniol was obtained in the form of a colorless liquid with a characteristic pleasant odor. Yield 6.3-6.5 g (87.5-90%).

B.p. 104-105° (6 mm), d_4^{22} 0.8862, n_D^{22} 1.4741, MR_D 49.98. $C_{10}H_{18}O\overline{F}_2$. Calc. 48.85.

Found %: active hydrogen 0.642 Calculated %: active hydrogen 0.649.

Preparation of citral (IV)

Preparation of active manganese dioxide. To a solution of 48 g potassium permanganate in 300 ml water, heated to 60-70°, was added with stirring, simultaneously from two dropping funnels, 34 g potassium hydroxide in 50 ml water and 45.5 g manganese sulfate in 40 ml water. Stirring was then continued with continuous cooling for 2 hours. The manganese dioxide was filtered through fabric, washed with distilled water until neutral, and dried at first in vacuum (20-30 mm) at 90-95° for 4 hours and then in a vacuum-desiccator over caustic alkali. Manganese dioxide was obtained in the form of a light-brown powder.

Oxidation. To a solution of 2.0 ml of the mixture of alcohols in 100 ml ligroine (b.p. 80-100°) was added 20 g manganese dioxide and the mixture shaken for 3 hours. The manganese dioxide was then filtered off and washed several times with ligroine on the filter. The ligroine was then driven off and the residue distilled in vacuum to give citral in the form of a faint-yellowish liquid with a characteristic odor. B.p. 96-97° (6 mm), n_D^{22} 1.4842. Yield 1.75-1.8 g (89-91%).

Citral semicarbazone. A solution of 0.5 g semicarbazide hydrochloride in 1.2 ml water was stirred with a solution of 0.4 g potassium acetate in 0.8 ml alcohol and run into a solution of 0.6 g citral in 1.2 ml alcohol. Crystallization commenced immediately on rubbing. After standing overnight in a refrigerator, the precipitate was filtered. Citral semicarbazone was obtained in the form of slightly yellowish crystals, m.p. 130-135°.

Found %: N 19.91. $C_{11}H_{19}ON_3$. Calculated %: N 20.09.

500 mg of the semicarbazone was dissolved in 5 ml anhydrous chloroform and put into a column with 25 g alumina (Brockmann activity II); elution was effected with chloroform, the movement of the substances in the column being observed from the fluorescence when illuminated with a mercury quartz lamp. The lower, most intense band was washed out completely after passage of 300 ml chloroform. A second band, considerably smaller, was washed out with the next 400 ml chloroform. After the chloroform had been distilled off, the dry residue was dissolved in hot methanol and filtered. After cooling, the crystals were filtered off. Neral

semicarbazone was obtained from the first eluate. M.p. 169-170°. Yield 230 mg. Similar working up of the second eluate gave a small (65 mg) amount of geraniol semicarbazone. M.p. 161-162°.

Methyl geranate (II). Dehydration with phosphorus oxychloride in pyridine

A mixture of 6.5 ml phosphorus oxychloride, 30 ml benzene and 30 ml pyridine was heated to the boil; addition was then made, with stirring, of a solution of 13.0 g of the hydroxy ester in 30 ml benzene; heating was carried out for 40-45 minutes; the mass was then cooled and poured on to ice, and the benzene layer was collected, washed with 5% sulfuric acid solution, with water and with bicarbonate solution before drying with sodium sulfate. After removal of the benzene, the residue was distilled in vacuum to give methyl geranate. B.p. 90-92° at 3 mm. Yield 6.8 g (58% reckoned on the methylheptenone).

A test for active hydrogen (Tserevitinov) was negative.

Reduction with lithium aluminum hydride. 3.6 g of the methyl ester of the dehydrated acid was run into a suspension of 0.9 g lithium aluminum hydride (90%) in 75 ml dry ether under the above-described conditions. The alcohol was obtained with b.p. 97-98° at 3 mm. Yield 2.7 g (89.0%).

Found %: active hydrogen 0.637. $C_{10}H_{18}O$. Calculated %: active hydrogen 0.649.

Oxidation with manganese dioxide. 1 g of the mixture of alcohols was oxidized under the above-described conditions with 10 g manganese dioxide in 50 ml ligroine. The solvent was removed and the residue was vacuum-distilled. B.p. 92-93° at 4 mm. Yield of citral 0.8 g (81%).

Test for active hydrogen (Tserevitinov) was negative.

SUMMARY

1. Condensation of methylheptenone with esters of bromoacetic acid followed by dehydration of the intermediate hydroxy ester by pyrolysis of the acetyl derivative or by the method of substitutive halogenation and removal of hydrogen halide gives esters of geranic acid.

2. Carbinols were synthesized from the esters, obtained by pyrolysis, by reduction of the carbalkoxyl group to the alcohol group; these carbinols correspond, according to the spatial arrangement of the substituents at the double bond, to nerol and geraniol.

3. Oxidation of the carbinols with activated manganese dioxide gave aldehydes which were identical with neral and geranial. Resolution of the semicarbazones indicates the predominance of neral in the mixture of aldehydes.

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CONFIGURATION AND PROPERTIES OF UNSATURATED ACIDS AND THEIR DERIVATIVES

IV. OXIDATION OF OCTADECENOIC ACIDS AND THEIR ESTERS BY BENZOYL HYDROPEROXIDE

A. K. Plisov and N. S. Skornyakova

This investigation was undertaken in order to determine the reactivity of the geometrically isomeric octadecenoic acids and of their esters. One of us has already shown to what extent the degree of reactivity of these compounds was associated with their steric configuration in the cases of hydrogenation, hydrolysis and oxidation with potassium permanganate [1, 2].

The results obtained confirmed the theory of one of us to the effect that the reactivity of unsaturated acids and of their derivatives must depend on their steric configuration. This was established by A. K. Plisov and E. G. Maleeva in a study of the oxidation of oleic and elaidic acids and their esters with an aqueous solution of potassium permanganate at the acid/oxidizing solution interface [3]. These investigations established that oxidation with potassium permanganate goes at different speeds in the cases of oleic and elaidic acids, and the introduction of an alcoholic radical with formation of an ester grouping lowers the reactivity. Employment of potassium permanganate, however, is inconvenient because oxidation takes place in several stages and continues up to rupture of the double bond; at the same time MnO_2 separates out and interferes with the study of the reaction course. These and other circumstances induced us to employ benzoyl hydroperoxide as the oxidizing agent in acetone solution.

The possibility of using organic per acids for preparation of oxygen compounds from unsaturated substances was discovered and exhaustively studied by the Russian chemist, N. A. Prilezhaev [4, 5].

We carried out oxidation in acetone solution because in this solution the reaction goes with measurable velocity and a solution of benzoyl hydroperoxide in pure acetone has adequate stability during the oxidation period.

Here we present data for the oxidation of the geometrically isomeric octadecenoic acids: oleic (cis-form), elaidic (trans-form), petroselenic (cis-form), petroselaidic (trans-form), and their esters (Table 1).

The naphthyl esters described here had not previously been prepared.

The results of oxidation confirmed the theory, proposed on the basis of the concept of steric hindrance, of the varying reactivity of geometrically isomeric unsaturated acids and their esters.

In all the cases of oxidation that we studied, the cis-forms were more active than the isomeric trans-forms. In addition it was established that the esters of the acids are considerably less active than the acids themselves. The size of the alcoholic radical is evidently here a determining factor.

EXPERIMENTAL

The oleic acid which we oxidized and which was also used for the preparation of elaidic acid esters was obtained from commercial oleic acid by suitable purification. Isomerization of oleic acid to elaidic acid was effected by heating at 210° with selenium.

Petroselinic acid was isolated from coriander oil and converted into petroselaidic acid by heating at 210° with selenium. The methyl esters were prepared by esterification in presence of H_2SO_4.

We used two methods for preparation of the β-naphthyl esters: reaction of potassium β-naphtholate with acid chlorides and reaction of β-naphthol with acid chlorides in presence of pyridine. Only β-naphthyl oleate was obtained in good yield by the first method; both esters were obtained in good yield by the second method. The constants of the compounds used in the oxidation experiments are set forth in Table 1.

TABLE 1

Constants of starting substances

Substance	Temperature		Acid number	Iodine number		Saponification number	
	of melting	of boiling		calculated	found by Hübl's method	calculated	found
Oleic acid	14.4°	222-223° (9 mm)	198.3	89.87	89.86	198.63	198.3
Elaidic acid	51	223-224 (9 mm)	198.5	89.87	89.87	198.63	198.5
Petroselinic acid	32.5	216-218 (8-9 mm)	198.6	89.87	89.8	198.63	198.6
Petroselaidic acid	54	–	198.5	89.87	89.89	198.63	198.5
Methyl oleate	–	190 (9 mm)	0.0	85.61	85.5	189.22	189.7
Methyl elaidate	–	191-192 (9 mm)	0.0	85.61	85.1	189.22	189.3
β-Naphthyl oleate	–	285-289 (9 mm)	0.0	62.12	61.9	137.31	137.2
β-Naphthyl elaidate	34	285-295 (9 mm)	0.0	62.12	63.1	137.31	136.0
Methyl petroselinate	–	158-160 (2-3 mm)	0.0	85.61	85.40	189.22	189.0
Methyl petroselaidate	–	164-165 (2-3 mm)	0.0	85.61	85.40	189.22	189.0

Oxidation of the acids and their esters was effected with benzoyl hydroperoxide in acetone solution. The hydroperoxide was prepared from benzoyl peroxide by the method described by Prilezhaev [5]. The concentration of the benzoyl hydroperoxide solution was determined from the content of active oxygen by the iodometric method. Oxidation was effected at constant temperature in a thermostat.

The course of the oxidation process was followed by measurement of the benzoyl hydroperoxide concentration at intervals.

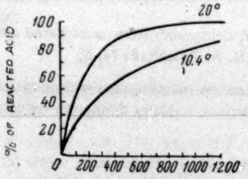

Fig. 1 Oxidation of oleic acid.

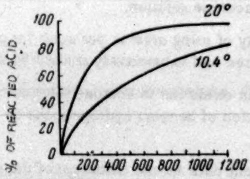

Fig. 2. Oxidation of elaidic acid.

The oxidizability of identical weights (1.0591 g) of oleic, elaidic, petroselinic and petroselaidic acids at 20 and 10.4° at a concentration of oxidizing agent of 0.3052 N, and at a concentration of the starting substance of 0.25 N are shown respectively in Table 2 and Fig. 1 and 2.

Determination of the oxidizability of equivalent amounts of the esters was carried out under the same conditions of temperature and concentration (Table 2 and Figs. 3-6).

In the summary graph (Fig. 7) is reflected the influence of the alcoholic radical on the oxidation of the esters at 20°. Results of oxidation of petroselinic acids and their esters are not shown in the graphs since they hardly differed from the corresponding data for oleic and elaidic acids and their esters.

The data of Table 2 and the graphs show that oleic and petroselinic acids are oxidized with appreciably greater facility than elaidic and petroselaidic acids. The same is true of the oxidation of the corresponding esters. Introduction of an ester group leads to a marked inhibition of the oxidation reaction and to an increase in the difference in the amounts of esters oxidized in comparison with acids after identical periods of time. Replacement of the methyl radical by naphthyl leads to a slight fall in the reactivity of the corresponding ester.

TABLE 2

Oxidation of octadecenoic acids and their esters

Name of substance oxidized	Duration of oxidation (in minutes)		% of substance oxidized	
	at 20°	at 10.4°	at 20°	at 10.4°
Oleic acid	1205	1347	99.8	87.5
Elaidic acid	1455	1347	99.0	80.5
Petroselinic acid	1200	1347	99.7	87.5
Petroselaidic acid	1450	1347	99.4	80.0
Methyl oleate	1200	1467	99.5	85.2
Methyl elaidate	1200	1467	95.0	75.3
Methyl petroselinate	1200	1465	99.6	85.2
Methyl petroselaidate	1200	1465	95.6	75.2
Naphthyl oleate	1200	1250	96.0	80.5
Naphthyl elaidate	1200	1260	89.0	71.3

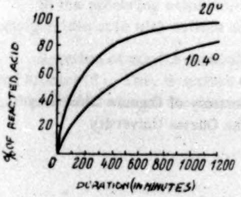

Fig. 3. Oxidation of Methyl oleate

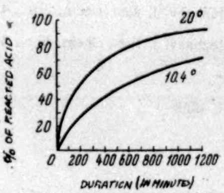

Fig. 4. Oxidation of Methyl elaidate

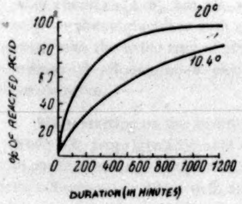

Fig. 5. Oxidation of β-Naphthyl oleate

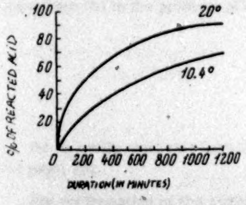

Fig. 6. Oxidation of β-Naphthyl elaidate

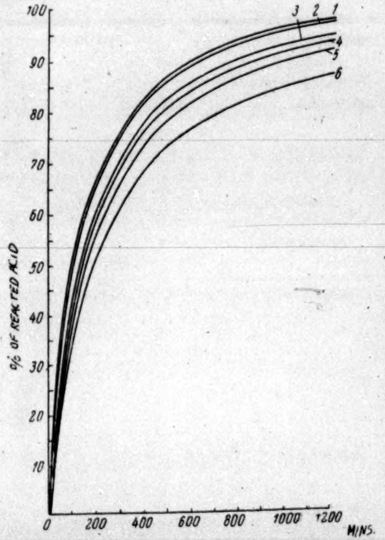

Fig. 7. Influence of the alcoholic radical upon the rate of oxidation. 1) oleic acid, 2) methyl oleate, 3) β-naphthyl oleate, 4) elaidic acid, 5) methyl elaidate, 6) β-naphthyl elaidate.

SUMMARY

1. β-Naphthyl oleate and β-naphthyl elaidate are synthesized for the first time and their properties described.

2. In oxidation with benzoyl hydroperoxide in acetone solution, oleic and petroselinic acids are oxidized more quickly than elaidic and petroselaidic acids.

3. The esters are oxidized more slowly than the corresponding acids; this effect is more marked with elaidates than with oleates.

4. Replacement of the methyl radical in the esters by naphthyl lowers the oxidation rate.

5. The results of the experiments on oxidation of oleic, elaidic, petroselinic and petroselaidic acids and their esters are in harmony with the theory of the influence of steric hindrance, and they illustrate the possibility of establishing by a chemical method whether a compound belongs to the cis- or to the trans-series.

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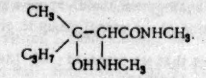
COMPOUNDS CONTAINING A THREE-MEMBERED RING

XV. STUDY OF THE REACTION OF THE ETHYL ESTER OF β-METHYL-β-PROPYLGLYCIDIC ACID WITH ANILINE

V. F. Martynov and Ya. A. Kastron

In the preceding communications [1, 2] we described the reaction of the ethyl ester of β-methyl-β-ethylglycidic acid with various aromatic amines. In the present paper we submit additional results in this field.

Reaction of ethyl β-methyl-β-propylglycidate with amines was studied by the French chemists Fourneau and Billeter [3]. They described the reaction of this ester with methylamine; without any evidence they assigned to the addition product the formula of the methylamide of α-methylamino-β-hydroxyisoenanthic acid (a):



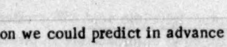
$$(CH_3)(C_3H_7)C(OH)-CH(NHCH_3)CONHCH_3$$

(a)

It must be pointed out that this formula is extremely improbable; it conflicts not only with the studies of other chemists [4, 5], but also with the latest studies of the same authors [6]. On investigating the reaction of ethyl β-phenylglycidate with aliphatic and aromatic amines, Fourneau and Billeter found that aliphatic amines break the oxide ring of glycidic acid from the side of the β-carbon atom with formation of amides of α-hydroxy-β-alkylamino-β-phenylpropionic acid, while aromatic amines break the ring from the side of the α-carbon atom.

When starting on the investigation we could predict in advance that the oxide ring in the ethyl ester of β-methyl-β-propylglycidic acid would be extremely stable and not readily susceptible to reaction due to the great steric hindrance of the substituents in the β-position. We therefore undertook the reaction of ethyl β-methyl-β-propylglycidate with aniline by heating not in a sealed ampoule, as we had done in the majority of such cases, but in an open flask at the boiling point of the mixture. In spite of these comparatively drastic conditions, we obtained a comparatively low yield of reaction product (30%).

On the basis of our preceding studies [1, 2] we could assign the formula of ethyl α-hydroxy-β-anilinoisoenanthate (b) to the products of interaction of the above components:



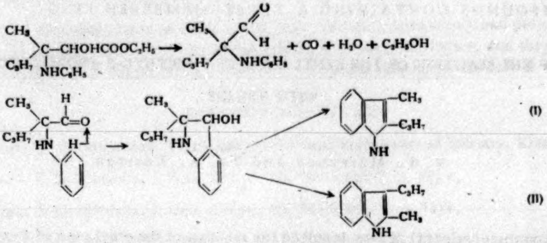
$$(CH_3)(C_3H_7)C(NHC_6H_5)-CHOHCOOC_2H_5$$

(b)

As is easily seen, this formula is in conflict with the claims of Fourneau and Billeter in their previously cited **paper [3]**

For confirmation of the correctness of our viewpoint, we subjected the addition product to the action of concentrated sulfuric acid with heating. At 100-105° we observed vigorous evolution of carbon monoxide; as we had previously shown, this is characteristic of α-hydroxy-β-arylamino acids. Consequently, it may be claimed that the conclusions of Fourneau and Billeter regarding the place of opening of the oxide ring of the above-mentioned glycidic acid under the action of methylamine are erroneous.

After detachment of the elements of formic acid, the remainder of the molecule is stabilized usually by transformation into the indole structure; in the present case methylpropylindole ought to have been obtained. Actually, we obtained a compound whose behavior corresponded to that of methylpropylindole; however, we could only guess its structure since two possible isomers could be formed in this reaction. The following scheme may be proposed:



As we see, two isomers could be formed if the retropinacoline rearrangement proceeding by condensation of the aldehyde group with the nucleus does not take place selectively.

In the two preceding papers [1, 2], in which we investigated the course of the retropinacoline rearrangement at two different radicals – methyl and ethyl – we established that the rearrangement goes selectively, i.e. the bigger radical (ethyl) changes its position. By analogy we could expect a selective pinacoline rearrangement also in the present case, with change of position of the propyl group to give 2-methyl-3-propylindole (II).

The melting point of the picrate of the indole that we prepared (133-134°) corresponded to the m.p. given in the literature for 2-methyl-3-propylindole – 134° [7].

For final confirmation we synthesized 2-methyl-3-propylindole by the Fischer method, prepared its picrate, and carried out a mixed melting test without obtaining a depression. Thus we actually had obtained 2-methyl-3-propylindole. The retropinacoline rearrangement went selectively with migration of the heavier radical.

EXPERIMENTAL

Synthesis of ethyl ester of β-methyl-β-propylglycidic acid. The ester was obtained by the Darzan method by reaction of methylpropyl ketone with ethyl chloroacetate in presence of sodium ethoxide. Yield 57%, allowing for the unreacted ethyl chloroacetate. After two distillations the b.p. was 96-97° at 12 mm.

d_4^{20} 0.9768, n_D^{20} 1.4279, MR_D 45.33; calc. 44.99.

Synthesis of ethyl ester of α-hydroxy-β-anilinoisoenanthic acid. A mixture of 34 g ethyl ester of β-methyl-β-propylglycidic acid and 55 g aniline was placed in a small flask fitted with a reflux condenser (ground-glass connection) to whose upper end was attached a Tishchenko bottle containing sulfuric acid. The mixture was heated at a gentle boil on Wood's alloy for 30 hours with intermissions. Toward the end of the heating the liquid in the flask had a cherry-red color.

In vacuum distillation a fraction was collected with b.p. 144-149° at 2 mm. The product was a viscous, light-yellow liquid which did not crystallize on standing. Yield 15 g (30%). After 2 redistillations b.p. 144-148° at 2 mm.

d_4^{20} 1.0643, n_D^{20} 1.5258. MR_D 76.50; calc. 74.64; EM 1.86.*

Found %: N 5.39 $C_{15}H_{23}O_3N$. Calculated %: N 5.28.

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* There are indications that alkyl-substituted anilines have an exaltation greater than unity [8].

Transformation of ethyl ester of α-hydroxy-β-anilinoisoenanthenic acid into 2-methyl-3-propylindole. To 11 g ethyl ester of α-hydroxy-β-anilinoisoenanthenic acid was added 50 ml concentrated sulfuric acid. The mixture was heated over a naked flame. At 95° carbon monoxide started to come off and the evolution became very intensive at 100-105°. The reaction continued for approximately an hour. After gas had ceased coming off, the red liquid was run into iced water, the acid was neutralized with caustic alkali, and the emulsified substance was extracted with ether. After the ether had been driven off, the product was fractionated in vacuum and the fraction with b.p. 127-130° at 3 mm was collected. 3 g golden yellow liquid was obtained with the characteristic indole odor; it turned red on standing. Yield 42%. After redistillation b.p. 127-128° at 2.5 mm.

d_4^{20} 1.0163, n_D^{20} 1.5778, MR_D 56.52; calc. 54.94, EM 1.58.

Found %: N 8.16. $C_{12}H_{15}N$. Calculated %: N 8.09.

A picrate was obtained in the form of small, cherry-red needles. After three recrystallizations and drying in vacuum the m.p. was 133-134°; the literature reports 134° [7]. No depression was obtained in a mixed melting test of the picrate of our preparation of 2-methyl-3-propylindole with the picrate of the same indole obtained by Fischer's method.

SUMMARY

1. The reaction of ethyl β-methyl-β-propylglycidate with aniline is studied. It is established that in this reaction the oxide ring of glycidic acid is opened from the side of the β-carbon atom.

2. The transition from ethyl-α-hydroxy-β-anilinoisoenanthate to 2-methyl-3-propylindole is effected. The case of a selective retropinacoline rearrangement was studied in this reaction. Of the two radicals (methyl and propyl), the heavier one migrates.

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* T. p. = C. B. Translation pagination.

Transformation of ethyl ester of α-hydroxy-β-[illegible] To 21 g ethyl ester of α-hydroxy-β-[illegible] was added 34 ml [illegible]. The mixture was heated over a naked flame. At 90° [illegible] rapidly increasing at 100-105°. The reaction continued for approximately an hour. After [illegible] of the red liquid was then poured into cold water, the acid was neutralized with [illegible] and the [illegible] substance was extracted with ether. After the ether had been driven off, the product was [illegible] and the fraction with b.p. [illegible] was collected. [illegible] pale yellow liquid [illegible] on standing. Yield [illegible]. After redistillation b.p. [illegible]

d_4^{20} 1.0186, n_D^{20} 1.5778, MR_D 59.82; calc. [illegible]

Found %: N 8.15. [illegible] Calculated %: N [illegible]

A picrate was obtained in the form of small [illegible]. After [illegible] in vacuum the m.p. was 136-138°; the literature reports [illegible] [7]. No depression was observed in a mixed melting test of the picrate of our preparation and [illegible] picrate of the same [illegible] by [illegible]'s method.

SUMMARY

1. The reaction of ethyl [illegible] with [illegible] the reaction the oxide ring of glycidic ester is opened from the side of the β-carbon atom.

2. The transition from ethyl [illegible] The [illegible] and propyl, the heavier [illegible].

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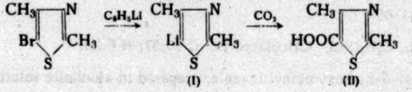
SYNTHESIS OF THIAZOLE DERIVATIVES WITH THE HELP OF ORGANOLITHIUM COMPOUNDS

B. M. Mikhailov and V. P. Bronovitskaya

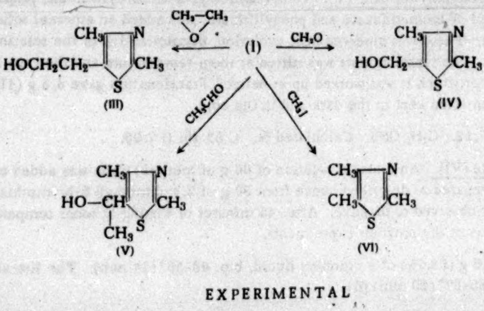
Organolithium compounds of thiazole are obtained both by the metalation reaction and by exchange of halogen by metal. By the first method lithium can be introduced into the 2-position of 4,5-dimethylthiazole by the action of phenyllithium [1]; the second method is applied, in particular, for the preparation of 2,4-dimethylthiazolyl-5-lithium from 2,4-dimethyl-5-bromothiazole and n-butyllithium [2].

We simplified the method of preparation of 2,4-dimethylthiazolyl-5-lithium (I) by replacing n-butyllithium by phenyllithium, and we used this lithium compound for the synthesis of some 5-derivatives of 2,4-dimethylthiazole.

Carboxylation of the lithium compound (I) leads to formation in good yield of 2,4-dimethylthiazole-5-carboxylic acid (II):



Reaction of organolithium compound (I) with ethylene oxide gave a 39% yield of 2,4-dimethyl-5-(β-hydroxyethyl)-thiazole (III); the latter had been obtained in very poor yield from β-bromoacetopropyl alcohol [3]. Condensation of 2,4-dimethylthiazolyl-5-lithium (I) with formaldehyde or acetaldehyde gave, respectively, 2,4-dimethyl-5-hydroxymethylthiazole (IV) or 2,4-dimethyl-5-α-hydroxyethylthiazole (V). Methyl iodide reacts smoothly with (I) to form 2,4,5-trimethylthiazole (VI):



EXPERIMENTAL

All operations with organolithium compounds were conducted in a nitrogen atmosphere.

2,4-Dimethylthiazole-5-carboxylic acid (II). To an ethereal solution of 0.516 g phenyllithium contained in a two-branched ampoule was gradually added an ethereal solution of 1 g 2,4-dimethyl-5-bromothiazole [4] with shaking and cooling with ice-salt mixture. After 15-minutes' shaking the reaction mixture was run on to solid carbon dioxide, and ether and water were added to the reaction products. Acidification of the aqueous layer led to separation of 0.6 g of an acid (73.5 %) with m.p. 223-225°; it was recrystallized from water; lustrous, white needles with m.p. 230-231°.

According to the literature 2,4-dimethylthiazole-5-carboxylic acid has m.p. 227° [5].

2,4-Dimethyl-5-(β-hydroxyethyl)-thiazole (III). To a solution of phenyllithium, prepared from 24 g bromobenzene, 2.1 g of lithium and 90 ml anhydrous ether, placed in a four-necked flask fitted with stirrer, reflux condenser, dropping funnel and nitrogen lead tube, was added with stirring and cooling with ice-salt mixture, an ethereal solution of 20 g 2,4-dimethyl-5-bromothiazole was gradually added. Gaseous ethylene oxide was passed into the dark-brown reaction mixture after 15 minutes' stirring. Lightening of the color of the solution and the formation of a voluminous light-yellow precipitate were observed.

At the conclusion of the reaction the alcoholate was decomposed with water, the ethereal solution was evaporated down, and the residue distilled in vacuum to give 6.36 g (39.2%) colorless oil with b.p. 130-132° (6 mm). According to the literature [3], 2,4-dimethyl-5-(β-hydroxyethyl)-thiazole melts at 130-131° (7-8 mm).

2,4-Dimethyl-5-hydroxymethylthiazole (IV). An ethereal solution of 30 g of 2,4-dimethyl-5-bromothiazole was added to a solution of phenyllithium, prepared from 36 g bromobenzene, 3.15 g lithium, and 135 ml of anhydrous ether. After 15 minutes, a stream of formaldehyde, obtained by depolymerization of paraformaldehyde, was passed into the reaction flask. The solution was decolorized and a voluminous precipitate formed.

The next day the reaction mixture was run into dilute hydrochloric acid containing ice, the lower, dark-brown layer was neutralized with concentrated ammonia solution, the resultant oil was extracted with chloroform, the solvent distilled off and the residue fractionated in vacuum.

There was obtained 14.3 g (64%) viscous, oily liquid with b.p. 123-125°, (4 mm), solidifying at room temperature to a crystalline mass with m.p. 43-45°.

Found %: C 50.59; H 6.42. C_6H_9ONS. Calculated %: C 50.31; H 6.33.

The picrate of 2,4-dimethyl-5-hydroxymethylthiazole, prepared in alcoholic solution, forms short, yellow needles with m.p. 106-107°.

Found %: C 38.56; H 3.04. $C_{12}H_{12}O_8N_4S$. Calculated %: C 38.70; H 3.25.

The hydrochloride of 2,4-dimethyl-5-hydroxymethylthiazole is formed by passing dry hydrogen chloride into an ethereal solution of the base; it crystallizes from anhydrous alcohol as colorless crystals with m.p. 151-153°, readily soluble in water and alcohol and insoluble in ether.

2,4-Dimethyl-5-α-hydroxyethylthiazole (V). To 2,4-dimethyl-5-thiazolyllithium, prepared as described above from 20 g 2,4-dimethyl-5-bromothiazole and phenyllithium, was added an ethereal solution of 9.2 g freshly distilled acetaldehyde. There was observed heat evolution, decolorization of the solution and separation of a light-yellow precipitate. The reaction mass was stirred at room temperature and then run into dilute hydrochloric acid and ice, after which it was worked up as before. Fractionation gave 6.8 g (41.5%) yellow oil, which easily decomposed even when kept in the dark and in the cold.

Found %: C 53.80; H 7.12. $C_7H_{11}ONS$. Calculated %: C 53.46; H 7.05.

2,4,5-Trimethylthiazole (VI). An ethereal solution of 66 g of methyl iodide was added to the 2,4-dimethyl-5-thiazolyllithium prepared as described above from 30 g of 2,4-dimethyl-5-bromothiazole and phenyllithium. The precipitate was observed to dissolve. After 45 minutes of stirring at room temperature, the reaction products were treated as in the previous experiments.

There was obtained 13.6 g (68.6%) of a colorless liquid, b.p. 48-50° (14 mm). The literature for 2,4,5-trimethylthiazole gives b.p. 65-67° (20 mm) [6].

The picrate of 2,4,5-trimethylthiazole with m.p. 135-136.5° is prepared from alcoholic solution. According to the literature, the picrate obtained from acidified aqueous solution has m.p. 133°.

SUMMARY

1. The lithium compound of 2,4-dimethylthiazole is smoothly obtained by the action of phenyllithium on 2,4-dimethyl-5-bromothiazole.

2. Starting from 2,4-dimethylthiazolyl-5-lithium, a series of 5-substituted derivatives of 2,4-dimethylthiazole was obtained.

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SUMMARY

1. The [illegible] of [illegible] is [illegible] by the [illegible] on 2,4-dimethyl-5-bromobenzoic acid.

2. Starting from 2,6-dimethyl[illegible], a series of ω-substituted derivatives of [illegible] was obtained.

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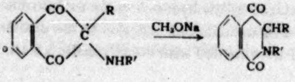
REACTION OF THE ETHYL ESTER OF CHLOROINDANEDIONECARBOXYLIC ACID WITH PRIMARY AMINES

G. Ya. Vanag and R. Ya. Silaraya

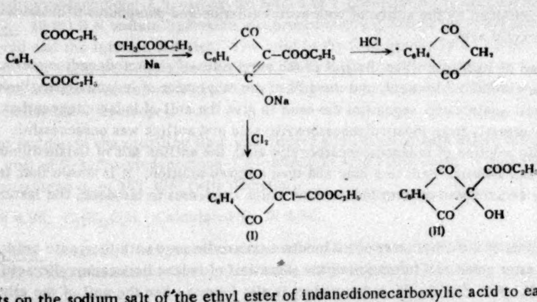
It is known that the halogen in the 2-position of indanedione-1,3 and in its homologs and derivatives is labile and easily replaced by other groups. Thus, for example, on acting upon 2-alkyl-2-bromoindanedione-1,3 with ammonia or amines, the corresponding derivatives of 2-aminoindanedione-1,3 are obtained [1]. Reaction of ammonia amines with 2-bromo-2-phenylindanedione-1,3 gives 2-amino-2-phenylindanediones-1,3. Under the influence of sodium methoxide these amino derivatives isomerize to the corresponding tetrahydroisoquinolines [2]:



Consequently a route is here opened up to transition from relatively easily accessible derivatives of the indane group to derivatives of isoquinoline.

Other cases of such a transition are also known. Thus, for example, Pfeiffer and coworkers [3-5] oxidized some derivatives of indanone and indanedione and likewise obtained isoquinoline derivatives. The Beckmann rearrangement of nitroindanedione oxime also gave an isoquinoline derivative [6, 7].

It was of interest to investigate also the possibility of transformation of simpler derivatives of indanedione into isoquinoline derivatives. As we know, indanedione-1,3 is obtained by decomposition with acid of the sodium salt of the ethyl ester of indanedionecarboxylic acid; the latter in turn is prepared by condensation of diethyl phthalate or, better still, dimethyl phthalate [8] with ethyl acetate in presence of metallic sodium.

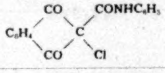


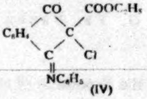
Chlorine acts on the sodium salt of the ethyl ester of indanedionecarboxylic acid to easily give the ethyl ester of chloroindanedionecarboxylic acid (I); the latter is consequently a most easily accessible halogen-substituted member of the indanedione group.

The chlorine atom in the ethyl ester of chloroindanedionecarboxylic acid is very labile; even with weak alkali, for instance, it is replaced by the hydroxyl group to form the ethyl ester of hydroxyindanedionecarboxylic acid (II) [9].

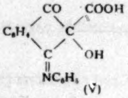
Phthalanil is obtained when the ethyl ester of chloroindanedionecarboxylic acid is heated with excess of aniline in the absence of a solvent. Formation of phthalanil when indanedione derivatives are treated with aniline has been repeatedly noted [10, 11]. It is also formed in solution in glacial acetic acid. When working in alcoholic solution, however, one can also isolate, apart from phthalanil, another reaction product in the form of white crystals with m.p. 115-116°. On further heating with aniline it is converted into phthalanil.

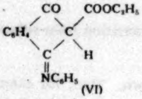
The isolated substance contains chlorine and nitrogen and, consequently, it may be either the anilide of chloroindanedionecarboxylic acid (III) or the anil of the ethyl ester of chloroindanedionecarboxylic acid (IV). The composition and properties are more consistent with the second formula.

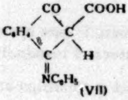

(III)


(IV)

The anil of the ethyl ester of chloroindanedionecarboxylic acid is very resistant to the action of mineral acids. On prolonged heating with semiconcentrated hydrochloric acid, only a small amount of resin is obtained; the main mass remains unchanged. By contrast, the anil reacts with facility with caustic alkalies, when the ester group is saponified and the chlorine is replaced by the hydroxyl group to form the anil of hydroxyindanedionecarboxylic acid (V). Ethanol was detected by the iodoform reaction in the distillate when the anil of the ethyl ester of chloroindanedionecarboxylic acid was distilled with dilute caustic alkali.


(V)


(VI)


(VII)

The compound obtained is an α-hydroxy acid. It is known that under the action of dilute sulfuric acid α-hydroxy acids are decomposed to form the corresponding aldehyde or ketone with cleavage of formic acid. In fact, on distilling the anil of hydroxyindanedionecarboxylic acid with dilute sulfuric acid, an acid distillate is obtained which reduces a solution of silver nitrate and of mercuric chloride. Pthalic acid crystallizes from the residue in the flask. Aniline is detected in the solution.

Only phthalanil is obtained by the action of both acetyl chloride and phosphorus trichloride on the anil of hydroxyindanedionecarboxylic acid.

Chlorine is replaced by hydrogen when the anil of the ethyl ester of chloroindanedionecarboxylic acid is reduced with zinc dust in glacial acetic acid, and the anil of the ethyl ester of indanedionecarboxylic acid (VI) is obtained. Caustic alkali again easily saponifies the ester to give the anil of indanedionecarboxylic acid (VII). An attempt to prepare it directly from indanedionecarboxylic acid and aniline was unsuccessful: on addition of aniline to the alcoholic solution of indanedionecarboxylic acid, the aniline salt of indanedionecarboxylic acid comes down; heating of the solution leads to a blue and then a brown solution. It is known that free indanedionecarboxylic acid is easily decomposed to form indanedione which condenses to biindone; the latter gives colored compounds with aniline.

Treatment of the anil of the ethyl ester of indanedionecarboxylic acid with inorganic acids likewise leads to saponification of the ester group and formation of the same anil of indanedionecarboxylic acid as in the saponification with alkali. And finally, the same product is also formed when the anil of the ethyl ester of indanedionecarboxylic acid is treated with hydriodic acid and red phosphorus.

m-Toluidine, α- and β-naphthylamines, etc. react like aniline with the ethyl ester of chloroindanedionecarboxylic acid. For example, on heating with m-toluidine without a solvent, only m-tolylphthalimide is formed;

but on heating in alcoholic solution both m-tolylphthalimide and the respective naphthalyphthalimides and a second reaction product analogous with the anil of the ethyl ester of chloroindanedionecarboxylic acid are obtained. With ethylamine only N-ethyl phthalimide is obtained. An intermediate reaction product could not here be isolated.

With secondary amines the formation of the corresponding anil of the ethyl ester of chloroindanedionecarboxylic acid is impossible. Heating of this ester with methylaniline without a solvent leads to a violent reaction with evolution of carbon dioxide and resinification. No reaction occurs when the same components are heated in ethereal solution, but chlorine is replaced by hydroxyl on heating in alcoholic solution with formation of the ethyl ester of hydroxyindanedionecarboxylic acid (II).

Consequently, we see here a rather unusual behavior of the ethyl ester of chloroindanedionecarboxylic acid. The chlorine of this compound is extremely easily replaced by the hydroxyl group although it could not be replaced by the amino group. It is known that indanedionecarboxylic acid is not a stable compound: on heating it easily splits off carbon dioxide and is transformed into indanedione. The anil of indanedionecarboxylic acid obtained in this investigation is stable and does not lose carbon dioxide. The anil of 2-hydroxyindanedionecarboxylic acid is likewise fairly stable.

EXPERIMENTAL

Action of aniline on the ethyl ester of 2-chloroindanedione-1,3-carboxylic acid-2. a) 1 g ethyl ester of the chloroindanedionecarboxylic acid and 3-4 ml aniline were boiled 10 minutes. The liquid turned dark-red. On cooling, the entire mass crystallized and 0.74 g phthalanil (84%) was obtained. M.p. 204-205°. It did not give a depression of melting point with pure phthalanil.

b) 10 g of the ethyl ester of the chloroindanedionecarboxylic acid was dissolved in 15 ml alcohol, 11 g aniline (3 moles aniline per mole ester) was added, and the mixture refluxed in a flask for 2 hours. On cooling, fine crystals of phthalanil came down – 3.23 g (37%). M.p. 205°. No depression of melting point with pure phthalanil.

Found %: N 6.40. $C_{14}H_9O_2N$. Calculated %: N 6.25.

The filtrate after separation of the phthalanil was acidified with dilute hydrochloric acid. Yellow-brown crystals came down. Yield 6.1 g (47.3%). Crystallization from benzene gave white platelets of the anil of the ethyl ester of chloroindanedionecarboxylic acid (IV) with m.p. 115-116°.

Found %: N 4.30; Cl 10.62. $C_{18}H_{14}O_3NCl$. Calculated %: N 4.27; Cl 10.82.

4 g of aniline was added to a solution of 1 g of the anil of the ethyl ester of chloroindanedionecarboxylic acid in 8 ml of alcohol, and the mixture was boiled for 3 hours. The liquid turned dark red. Upon cooling, a crystalline precipitate of phthalanil came down in a yield of 0.55 g (80.9%). After crystallization from alcohol it had m.p. 205°. With pure phthalanil it gave no melting point depression.

Anil of 2-hydroxyindanedione-1,3-carboxylic acid-2 or 1-phenylimino-2-hydroxyindanedione-3-carboxylic acid-2 (V). 40 ml 3 N sodium hydroxide was poured over 3 g anil of the ethyl ester of chloroindanedionecarboxylic acid and the mixture distilled. The solid in the flask gradually dissolved. A colorless distillate with a faint odor of aniline was obtained. A little dilute sulfuric acid was added to it and the mixture again distilled. The distillate contained ethyl alcohol and gave a pronounced iodoform reaction (odor, characteristic crystals under the microscope).

The alkaline residue in the distilling flask was filtered and acidified with dilute sulfuric acid. A white precipitate of the anil of 2-hydroxyindanedione-1,3-carboxylic acid came down. Yield 1.65 g (63.5%). After crystallization from xylene m.p. 167-168° (with decomp.).

Found %: N 4.92. $C_{16}H_{11}O_4N$. Calculated %: N 4.98.

Ammonium salt. Ammonia was poured over the anil of 2-hydroxyindanedionecarboxylic acid. The compound dissolved. The ammonium salt was obtained by evaporating the solution.

Found %: N 9.25. $C_{16}H_{14}O_4N_2$. Calculated %: N 9.40.

Dilute sulfuric acid (1 : 5) was poured over the anil of 2-hydroxyindanedionecarboxylic acid. On distillation an acid distillate was obtained with the characteristic reactions of formic acid: it reduced silver nitrate and mercuric chloride. When the residue in the flask was cooled, phthalic acid came down (it sublimed in the form of phthalic anhydride with m.p. 128°; the sublimate gave the fluorescein reaction). To the filtrate was added excess of sodium hydroxide and the mass extracted with ether. Evaporation of the ether left oily drops of aniline (violet coloration with bleaching powder).

Anil of the ethyl ester of indanedione-1,3-carboxylic acid-2 or the ethyl ester of 1-phenyliminoindanedione-3-carboxylic acid-2 (VI). 2 g of the anil of the ethyl ester of chloroindanedionecarboxylic acid was dissolved in 20 ml glacial acetic acid, zinc dust was added and the mixture boiled 1-2 hours. After filtration the filtrate was diluted with water. A grey precipitate of the anil of the ethyl ester of indanedionecarboxylic acid came down. Yield 1.2 g (66.6%). After a few recrystallizations from alcohol the m.p. was 109-110°.

Found %: N 5.25. $C_{18}H_{15}O_3N$. Calculated %: N 4.77.

Aniline salt of the ethyl ester of indanedionecarboxylic acid. 1 ml of aniline was added to a solution of 1 g of the ethyl ester of indanedionecarboxylic acid [12] in 10 ml alcohol. The liquid became an intense yellow, and coarse, yellow, cubical crystals of the aniline salt of the ethyl ester of indanedionecarboxylic acid gradually separated out. M.p. 100° (with decomp.).

Found %: N 4.64. $C_{18}H_{17}O_4N$. Calculated %: N 4.50.

Carbon dioxide came off when the aniline salt was heated with dilute hydrochloric acid, and indanedione came down. M.p. 128°. No melting point depression with pure indanedione.

Anil of indanedionecarboxylic acid or 1-phenyliminoindanone-3-carboxylic acid-2 (VII). a) 1 g anil of the ethyl ester of indanedionecarboxylic acid was covered with 20 ml 3 N sodium hydroxide and distilled. The solid gradually went into solution. The colorless distillate had a faint odor of aniline. After addition of a little dilute sulfuric acid, the material was again distilled. Ethyl alcohol was detected in the distillate by the iodoform reaction. The alkaline residue in the distillation flask was filtered and acidified with dilute hydrochloric acid. A white precipitate of the anil of indanedionecarboxylic acid came down. Yield 0.8 g. M.p. 190°; after recrystallization from benzene it had m.p. 192-193°. It was soluble in sodium bicarbonate.

Found %: N 5.31. $C_{16}H_{11}O_3N$. Calculated %: N 5.28.

b) The anil of the ethyl ester of [illegible] indanedionecarboxylic acid was boiled with hydrochloric acid (1:1). The anil of the ester at first floated in the liquid in the form of oily drops and then converted to a white precipitate of the anil of indanedionecarboxylic acid. After crystallization from benzene it had m.p. 192-193°.

Found %: N 5.21. $C_{16}H_{11}O_3N$. Calculated %: N 5.28.

c) 5 g of the ethyl ester of indanedionecarboxylic acid, 5 g red phosphorus and 15 ml commercial hydriodic acid were refluxed in a flask for 30 minutes. The hot solution was suction-filtered through a glass filter. A yellow precipitate came down on cooling. It was diluted with water, and suction-filtered. Yield 2.6 g of the anil of indanedionecarboxylic acid. M.p. 192-193°.

Found %: N 5.27. $C_{16}H_{11}O_3N$. Calculated %: N 5.28.

Action of m-toluidine on the ethyl ester of chloroindanedionecarboxylic acid. [illegible] of the ethyl ester of chloroindanedionecarboxylic acid was boiled with an excess of m-toluidine for 5-10 minutes. The liquid turned dark red. Upon cooling m-tolylphthalimide precipitated out. Yield 1.5 g. After crystallization from glacial acetic acid m.p. 170-172°. The mixture with pure m-tolylphthalimide melts without depression.

5 g of the ethyl ester of chloroindanedionecarboxylic acid was dissolved in 10 ml alcohol and 4 g m-toluidine was added. The mixture was boiled 2 hours. On cooling, 0.8 g m-tolylphthalimide came down. M.p. 170-172°.

Found %: N 6.10. $C_{15}H_{11}O_2N$. Calculated %: N 5.91.

To the filtrate was added dilute hydrochloric acid until the reaction was acidic. The ethyl ester of 1-m-tolylimino-2-chloroindanone-3-carboxylic acid-2 was precipitated (IV, m-$C_6H_4CH_3$ instead of C_6H_6). Yield 4.25 g. After crystallization from carbon tetrachloride m.p. 143-145°.

Found %: N 4.30. $C_{19}H_{16}O_3NCl$. Calculated %: N 4.10.

2 ml of m-toluidine was added to a solution of 0.3 g of the ethyl ester of 1-m-tolylimino-2-chloroindanone-3-carboxylic acid-2 in 6 ml of alcohol and the mixture was boiled for 3 hours. After cooling, dilute hydrochloric acid was added. 0.18 g of m-tolylphthalimide precipitated out. After crystallization from glacial acetic acid it had m.p. 170-172°. With pure m-tolylphthalimide it gave no melting point depression.

Action of β-naphthylamine on the ethyl ester of chloroindanedionecarboxylic acid. 5 g of the ethyl ester of chloroindanedionecarboxylic acid, 5.3 g of β-naphthylamine and 10 ml of alcohol were boiled for 2 hours. Upon cooling 0.8 g of β-naphthylphthalimide precipitated out of the solution. After crystallization from glacial acetic acid, it formed colorless needles with m.p. 217-219°.

Found %: N 3.98. $C_{18}H_{11}O_2N$. Calculated %: N 3.75.

Crystals with m.p. 158-160° came down from the filtrate after separation of the β-naphthylphthalimide on standing in an open vessel. After crystallization from alcohol the ethyl ester of 1-(β-naphthylimino)-2-chloroindanone-3-carboxylic acid-2 was obtained in the form of white crystals with m.p. 172-174°.

Found %: N 3.33. $C_{22}H_{16}O_3NCl$. Calculated %: N 3.70.

Action of α-naphthylamine on the ethyl ester of chloroindanedionecarboxylic acid. 5 g ethyl ester of chloroindanedionecarboxylic acid, 5.3 g of α-naphthylamine and 10 ml of alcohol were boiled for 2 hours. Upon cooling, 3.7 g of α-naphthylphthalimide precipitated out. After crystallization from alcohol, colorless crystals formed, m.p. 180-181°.

Found %: N 3.95. $C_{18}H_{11}O_2N$. Calculated %: N 3.75.

Action of ethylamine on the ethyl ester of chloroindanedionecarboxylic acid. 3 g ethyl ester of chloroindanedionecarboxylic acid was covered with 5 ml 33% ethylamine solution. The compound quickly dissolved, heat was evolved and the color changed to dark-red. The mass was boiled 10 minutes. Crystals of N-ethylphthalimide came down on cooling. Yield 1.7 g (80.9%). Crystallization from alcohol gave long needles with m.p. 76-78°.

Found %: N 7.91. $C_{10}H_9O_2N$. Calculated %: N 8.00.

The corresponding ethylimine could not be isolated in this case.

Reaction of the ethyl ester of chloroindanedionecarboxylic acid with methylaniline. 3 g of the ethyl ester of chloroindanedionecarboxylic acid, 10 ml of alcohol and 2.5 g of methylaniline were boiled for 2 hours. On cooling, crystals of the ethyl ester of 2-hydroxyindanedione-1,3-carboxylic acid-2 (II) came down. Yield 0.6 g. After crystallization from alcohol m.p. 120°. From the filtrate after addition of dilute hydrochloric acid before solution of the methylaniline was isolated a further 0.2 g ethyl ester of hydroxyindanedionecarboxylic acid. M.p. 120°. No melting point depression with the pure compound.

SUMMARY

Reaction of aniline with the ethyl ester of chloroindanedionecarboxylic acid gives, depending upon the conditions, either only phthalanil or a mixture of the latter with the anil of the above ester. When the prepared anil of the ethyl ester of chloroindanedionecarboxylic acid is saponified, its chlorine is simultaneously replaced by hydroxyl and the anil of hydroxyindanedionecarboxylic acid is formed. Reduction of the anil of the ethyl ester of chloroindanedionecarboxylic acid gives the anil of the ethyl ester of indanedionecarboxylic acid which is saponified to the anil of indanedionecarboxylic acid. The phenylimino group in all these anils is very firmly bound and is split off only when the molecule is completely cleaved. Reaction of methylaniline with the ethyl ester of chloroindanedionecarboxylic acid gives the ethyl ester of hydroxyindanedionecarboxylic acid. Thus the chlorine in the ethyl ester of chloroindanedionecarboxylic acid is easily replaced by hydroxyl, although it could not be replaced by the amino group.

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MIXED ESTERS OF ARYLSULFONIMIDOPHOSPHORIC ACIDS AND NON-ROTATIONAL TETRAHEDRAL ISOMERISM

A. V. Kirsanov and V. I. Shevchenko

The nature of the bond between the atoms of nitrogen and phosphorus in phosphazo compounds has hitherto been unclarified. This bond may be single and completely polarized ($-N^- - P^+\equiv$), it may be double ($-N=P\equiv$) and finally, what is more probable, it may be double and partly polarized ($-N^{-\delta}=P^{+\delta}\equiv$). In the first case (single bond) compounds of the type of $ArSO_2N^- - P^+(RR'R'')$ must exist in the form of two optically active antipodes and one racemic compound, while compounds of the type of $ArSO_2N^-=P^+(RRR')$ cannot have isomers. In the second case (double bond) rotation round the N–P axis becomes impossible, and a new form of isomerism is developed which is a combination of optical and a special type of cis-trans isomerism. Since this form of isomerism is caused by hindrance to rotation of the tetrahydedron formed by the substituents at the phosphorus atom, it should be called "non-rotational tetrahedral isomerism". In the case of a double bond between the atoms of nitrogen and phosphorus, compounds of the type of $ArSO_2N=P(RR'R'')$ (I) must exist in the form of six optically active isomers and three racemates, and compounds of the type of $ArSO_2N=P(RRR')$ (II) in the form of two optically active isomers, one racemate and one meso compound. In the case of partial polarization the number of isomers of compounds of types (I) and (II) will depend upon the magnitude of the energy of activation of rotation round the N–P axis, i.e. upon the degree of polarization of the $-N=P\equiv$ bond. Consequently, by studying compounds of the type of (I) and (II) we may hope to elucidate the character of the bond between the nitrogen and phosphorus atoms in phosphazo compounds.

The simplest and most easily accessible compounds of type (I) and (II) are mixed esters of arylsulfonimidophosphoric acids of the type of $ArSO_2N=P(OR)(OR')(OR'')$ (III) and $ArSO_2N=P(OR)_2(OR')$ (IV) and related compounds. For the preparation of esters of types (III) and (IV) it might have appeared simplest to start from trichlorophosphazo compounds and gradually replace the chlorine atoms by various OR groups. As preliminary experiments revealed, this method is associated with great experimental difficulties since the intermediate products of the types of $ArSO_2N=PCl_2(OR)$ and $ArSO_2N=PCl(OR')(OR)$ do not distill without decomposition and cannot be obtained in the crystalline state. Compounds of types (III) and (IV) were therefore prepared by a method which had previously been successfully applied to the preparation of trichlorophosphazosulphonaryls [1] and triarylphosphazosulfonaryls [2]; this is the action of sodium salts of chloroamides of sulfonic acids upon the appropriate compounds of trivalent phosphorus according to the scheme:

$$ArSO_2NNaCl + P(OR)(OR')(OR'') \longrightarrow NaCl + ArSO_2N=P(OR'')(OR')(OR).$$

For verification of the applicability of the method, triphenyl phosphite was reacted with sodium salts of chloroamides of benzene sulfonic acid and naphthol sulfonic acids. Very good yields were then obtained of the triphenyl esters of the corresponding arylsulfonimidophosphoric acids which proved to be identical with the products obtained by phenoxylation of the corresponding trichlorophosphazosulfonaryls [3].

For preparation of mixed aromatic esters of arylsulfonimidophosphoric acids, the following, previously undescribed, mixed esters of phosphorous acid were synthesized: o,m-dicresylphenyl phosphite, o,p-dicresylphenyl phosphite, and m,m-dicresylphenyl phosphite. All these, like the triphenyl ester of phosphorous acid, react easily with sodium salts of chloroamides of benzene and β-naphthalene sulfonic acids. These esters (as also triphenyl phosphite) react with very great difficulty with the sodium salt of the chloroamide of α-naphthalene sulfonic acid.

In all, five mixed esters of phenyl-, o-tolyl- and β-naphthylsulfonimidophosphoric acids were obtained.

All were obtained in yields close to the theoretical; 4 of them are thick, viscous liquids which have not so far been isolated in crystalline form or resolved into fractions of the same composition. It is therefore impossible to draw any conclusions as to whether they are individual substances or mixtures of racemates. However, one of the esters, namely the o,m-dicresylphenyl ester of phenylsulfonimidophosphoric acid $C_6H_5SO_2N=$ $=P(OC_6H_5)(OC_6H_4CH_3\text{-}o)(OC_6H_4CH_3\text{-}m)$ (V), obtained in 97.4% yield in the form of a viscous, nearly colorless liquid, deposits over 25 %crystalline substance with m.p. 57-59° after standing for many days. Both the liquid and the crystalline substance have the composition and chemical properties corresponding to ester (V). Evidently the solid substance is one of the three theoretically possible racemates (V), while the liquid is a mixture of racemates (IV). This assumption is confirmed by the synthesis of the triphenyl ester of phenylsulfonimidophosphoric acid, $C_6H_5SO_2N=P(OC_6H_5)_3$, which is obtained under identical conditions in 97.6 % yield in the very pure state. There are no reasons for believing that o,m-dicresylphenyl phosphite (VI) would react with the sodium salt of the chloroamide of benzene sulfonic acid (VII) in a manner fundamentally different from that of triphenyl phosphite, and it should therefore give neutral substances of the same composition as (V) but with fundamentally different structures. Hence it follows that the liquid and crystalline products of reaction of (VI) and (VII) can only be isomers of (V), and that non-rotational tetrahedral isomerism apparently exists. A final solution of this problem must await further experiments on other aspects.

The properties of esters of the types of (III) and (IV) are described in the experimental section.

EXPERIMENTAL

Reaction of sodium salts of chloroamides of aromatic sulfonic acids with esters of phosphorous acid. The speed of reaction of sodium salts of chloroamides of aromatic sulfonic acids with triphenyl phosphite depends upon the aromatic residue of the sulfonic acid. The sodium salt of the chloroamide of benzene sulfonic acid reacts very vigorously with triphenyl phosphite with much evolution of heat and resinification of the reaction product. For avoidance of resinification the reaction must be conducted under milder conditions in presence of solvents. The salt of the chloroamide of β-naphthalene sulfonic acid reacts less energetically. The sodium salt of the chloroamide of α-naphthalene sulfonic acid reacts very sluggishly with triphenyl phosphite. The reaction does not go even with heating on a water bath. The reaction velocity depends to a still greater extent upon the character of the phosphazo-containing compound. Thus, whereas the sodium salt of the chloroamide of α-naphthalene sulfonic acid reacts very energetically with phosphorus trichloride, with the dichloroanhydride of the phenyl ester of phosphorous acid the reaction goes perfectly quietly, with the chloroanhydride of diphenyl phosphite the reaction only goes on heating, and with triphenyl phosphite the reaction does not go even at 100°.

Mixed esters were prepared by introducing into a 50 ml flask 0.01 mole ester of phosphorous acid and 5 ml carbon tetrachloride, heating the mixture to 50° and adding in several portions (0.5 g each) 0.01 mole anhydrous sodium salt of the chloroamide previously pulverized to a fine powder. 50 ml carbon tetrachloride was run into the reaction mixture which was then stood for a few hours. The sodium chloride came out and was separated easily. The filtrate was evaporated (the carbon tetrachloride was taken off in vacuum) on a water bath. The triphenyl esters came down in the crystalline form even while the solvent was being distilled off. The mixed phenylcresyl esters are obtained in the form of viscous, transparent, oily liquids, which are nearly colorless or faint yellow.

The following esters were prepared in this manner:

The triphenyl ester of phenylsulfonimidophosphoric acid $C_6H_5SO_2N=P(OC_6H_5)_3$, yield 4.53 g (97.6%). After one recrystallization from alcohol m.p. 85-86°. A mixed sample with the triphenyl ester prepared from trichlorophosphazosulfonphenyl and sodium phenolate did not give a depression of melting point.

Triphenyl ester of β-naphthylsulfonimidophosphoric acid $\beta\text{-}C_{10}H_7SO_2N=P(OC_6H_5)_3$, yield 4.76 g (92.4%). After crystallization from alcohol m.p. 90-91°. A mixed sample with the ester prepared from β-trichlorophosphazosulfonaphthyl and sodium phenolate did not give a depression of melting point.

m,m-Dicresylphenyl ester of phenylsulfonimidophosphoric acid, $C_6H_5SO_2N=P(OC_6H)(OC_6H_4CH_3\text{-}m)_2$, yield 4.8 g (97.4%). A viscous, non-crystallizing, oily liquid. At room temperature it is miscible in all proportions with benzene, acetone, alcohol, carbon tetrachloride and ether; insoluble in water and ligroine.

Found %: N 2.69, 2.68. $C_{26}H_{24}O_5NSP$. Calculated %: N 2.84.

o,p-Dicresylphenyl ester of phenylsulfonimidophosphoric acid, $C_6H_5SO_2N=P(OC_6H_5)(OC_6H_4CH_3\text{-}o)$- $\text{-}(OC_6H_4CH_3\text{-}p)$, yield 4.87 g (98.7%). A viscous, transparent, non-crystallizing liquid. Mixes in all proportions with benzene, acetone, alcohol and ether. Insoluble in water and ligroine.

Found %: N 2.70, 2.72. $C_{26}H_{24}O_5NSP$. Calculated %: N 2.84.

o,m-Dicresylphenyl ester of o-tolylsulfonimidophosphoric acid, $o\text{-}CH_3C_6H_4SO_2N= = P(OC_6H_5)(OC_6H_4CH_3\text{-}o)(OC_6H_4CH_3\text{-}m)$, yield 97.4%. Viscous liquid. Was not analyzed.

o,m-Dicresylphenyl ester of β-naphthylsulfonimidophosphoric acid, $\beta\text{-}C_{10}H_7SO_2N= = P(OC_6H_5)(OC_6H_4CH_3\text{-}o)(OC_6H_4CH_3\text{-}m)$, yield 92.4%. Viscous liquid. Was not analyzed.

o,m-Dicresylphenyl ester of phenylsulfonimidophosphoric acid, $C_6H_5SO_2N= = P(OC_6H_5)(OC_6H_4CH_3\text{-}o)(OC_6H_3CH_3\text{-}m)$, yield 4.80 g (97.4%). A viscous, oily liquid.

Found %: N 2.68, 2.75. $C_{26}H_{24}O_5NSP$. Calculated %: N 2.84.

The ester slowly crystallizes on standing and is gradually converted into a semicrystalline slurry. For isolation of the crystalline portion, the product was dissolved in a small amount of alcohol and cooled in a mixture of snow and salt. An oily layer was formed which readily crystallized (sometimes only after prolonged cooling). The crystals were collected and thoroughly pressed between sheets of filter paper. The substance comes down from ligroine in the form of long, slender needles radiating from a single point, m.p. 57-59°. Yield 25-35% of the total mass. The crystals, also the liquid product, are very soluble in alcohol, acetone, benzene, carbon tetrachloride and ether; insoluble in water and cold ligroine, difficultly soluble in hot ligroine (about 0.1 g in 100 ml).

Found %: N 2.82, 2.94. $C_{26}H_{24}O_5NSP$. Calculated %: N 2.84.

Chemically the mixed aromatic esters are stable substances with properties like those of the triphenyl and tricresyl esters [3]. On alkaline hydrolysis the mixed phenylcresyl esters are saponified with the same ease as the phenyl or the cresyl ester groups with formation of mixtures of acid esters.

Preparation of mixed esters of phosphorous acid. A stream of dry carbon dioxide was passed at room temperature through a mixture of 0.5 mole phenyl phosphite dichloroanhydride (97.5 g) and 0.5 mole of the appropriate cresol for 3 hours. The mixture was then heated on a boiling water bath for 1 hour without interrupting the flow of carbon dioxide. When evolution of hydrogen chloride had ceased, the mixture was twice distilled in a column in vacuum. A first fraction boiling within a 5° range was collected, and a second fraction boiling within 2-3°.

The prepared monochloroanhydrides of the cresylphenyl phosphites were subjected to the same treatment in the case of each cresol. Yield about 80%.

All the intermediate products and all the mixed esters of phosphorous acid prepared by this method are viscous, colorless liquids. o,m-Dicresylphenyl phosphite, b.p. 215-217° at 5 mm; o,p-dicresylphenyl phosphite, b.p. 212-214° at 5 mm; m,m-dicresylphenyl phosphite, b.p. 210-215° at 4 mm; chloroanhydride of m-cresylphenyl phosphite, b.p. 158-159° at 5 mm; chloroanhydride of p-cresylphenyl phosphite, b.p. 153-154° at 4 mm.

SUMMARY

1. The question of the existence of non-rotational tetrahedral isomerism is posed.

2. Mixed esters of arylsulfonimidophosphorous acids are prepared.

3. The o,m-dicresylphenyl ester of phenylsulfonimidophosphoric acid is obtained in the form of two isomers – a liquid and a crystalline substance; this may be attributed to non-rotational tetrahedral isomerism.

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I. V. Stalin Dnepropetrovsk Institute
of Metallurgy

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* T. p. = C. B. Translation pagination.

[illegible] benzene, acetone, [illegible] and [illegible], insoluble in water and ligroin.

Found %: N [illegible]. [illegible]. Calculated %: N [illegible].

[illegible]

[illegible] analysis.

[illegible]

[illegible]

[illegible]

Found %: N [illegible]. Calculated %: N [illegible].

[illegible] converted into a [illegible] crystalline mass. [illegible] was dissolved in a small amount of [illegible] and [illegible] crystallized immediately only after strongly [illegible] mixture of snow and salt. [illegible] between strips of filter paper. The substance [illegible] single crystal [illegible]. Yield [illegible] of the total mass. The crystals [illegible] soluble in alcohol, acetone, [illegible] sparingly soluble in the ligroin [illegible].

Found %: [illegible]. Calculated %: [illegible].

[illegible] with the same [illegible] and [illegible].

[illegible] was placed [illegible] and [illegible] of [illegible]. [illegible] the [illegible] ceased, the [illegible], and a second [illegible].

The prepared [illegible] were subjected to the same treatment [illegible].

All the [illegible] by the method [illegible] phenyl [illegible] of the [illegible].

SUMMARY

1. The [illegible].

2. [illegible].

3. The [illegible].

LITERATURE CITED

[1] A. V. Kirsanov, J. Gen. Chem. 22, [illegible] (1952).*

[2] A. V. Kirsanov [illegible].

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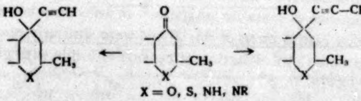
ACETYLENE DERIVATIVES

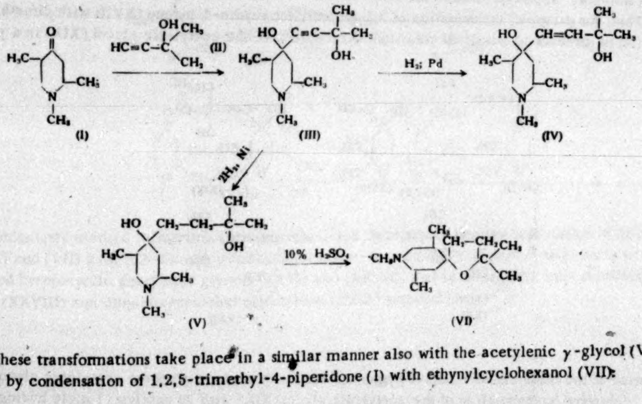
170. HETEROCYCLIC COMPOUNDS. XXXI. SYNTHESIS AND TRANSFORMATIONS OF HETEROCYCLIC ACETYLENIC γ-GLYCOLS

I. N. Nazarov and L. N. Ivanova

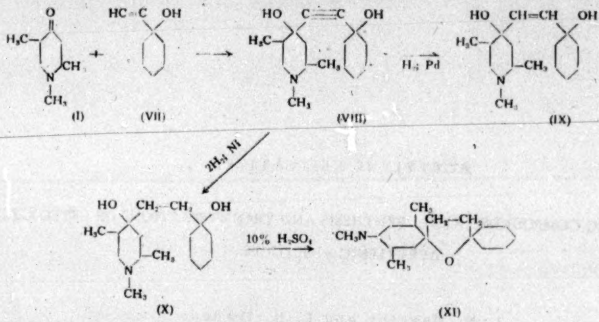
Some years ago in our laboratory the condensation was realized of acetylene and of vinylacetylene with various heterocyclic ketones (tetrahydro-γ-pyrones, tetrahydro-γ-thiopyrones, γ-piperidones), and in this way the corresponding heterocyclic acetylenic and vinylacetylenic alcohols were obtained for the first time [1-3].


HO C≡CH
CH₃
X
O
CH₃
X
HO C≡C—CH=CH₂
CH₃
X
X = O, S, NH, NR

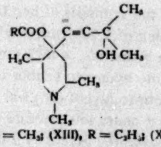
It appeared of interest to apply this condensation also to the synthesis of heterocyclic acetylenic γ-glycols, which had not hitherto been investigated at all. On condensation of 1,2,5-trimethyl-4-piperidone (I) with dimethylethynylcarbinol (II) in presence of pulverized potassium hydroxide, a 60% yield of the unsymmetrical acetylenic γ-glycol (III) was obtained. After addition of 1 mole hydrogen to this acetylenic glycol in presence of Pd catalyst, hydrogenation slowed down abruptly and the olefinic glycol (IV) was formed. Exhaustive hydrogenation of the acetylenic glycol (III) in presence of Ni catalyst under low pressure of hydrogen (8-10 atm.) at room temperature led to nearly quantitative formation of the saturated glycol (V); heating of the latter with 10% sulfuric acid gave about 90% yield of the tetrahydrofuran derivative (VI):

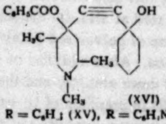

O
H₃C
CH₃
N
CH₃
(I)
OH CH₃
HC≡C—C
CH₃
(II)
HO C≡C—C—CH₃
CH₃
OH
H₃C
CH₃
N
CH₃
(III)
H₂; Pd
HO CH=CH—C—CH₃
CH₃
OH
H₃C
CH₃
N
CH₃
(IV)
2H₂, Ni
HO CH₂—CH₂—C—CH₃
CH₃
OH
H₃C
CH₃
N
CH₃
(V)
10% H₂SO₄
CH₃
CH₂—CH₂
CH₃
CH₃N
C
O
CH₃
CH₃
(VI)

All these transformations take place in a similar manner also with the acetylenic γ-glycol (VIII), which is obtained by condensation of 1,2,5-trimethyl-4-piperidone (I) with ethynylcyclohexanol (VII):



The prepared tetrahydrofuran derivatives (VI) and (XI) contain a piperidine and tetrahydrofuran ring linked by a common spiroatom of carbon. A similar link between these rings is also found in the morphine molecule. Physiological tests of the crystalline methoiodides showed, however, that these preparations do not possess a sedative action. Esterification of the acetylenic glycols (III) and (VIII) with acid chlorides by the method of Spassow [4] gave a series of monoesters for pharmacological investigations. Thus, by the action of acetyl chloride upon glycol (III) in presence of metallic magnesium in anhydrous benzene, a 63% yield of the monoacetate (XII) was obtained. Other partial esters of this glycol were similarly prepared – the propionate (XIII), benzoate (XIV) and p-nitrobenzoate (XV). Reaction of benzoyl chloride with glycol (VIII) gave under similar conditions the monobenzoate (XVI):

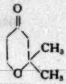




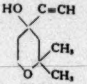
(XVI)

(XII), $R = CH_3$; (XIII), $R = C_2H_5$; (XIV), $R = C_6H_5$; (XV), $R = C_6H_4NO_2$-*n*

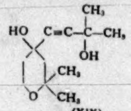
Condensation of the acetylenic alcohols (II) and (VII) with tetrahydro-γ-pyrones and tetrahydro-γ-thiopyrones goes less smoothly, apparently due to the lower stability of these heterocyclic ketones in presence of caustic alkali. Thus, for example, condensation of 2,2-dimethyltetrahydro-4-pyrone (XVII) with dimethylethynylcarbinol (II) in presence of powdered potassium hydroxide gave the acetylenic glycol (XIX) in a yield of only 30%.



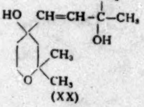
(XVII)



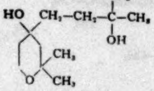
(XVIII)



(XIX)

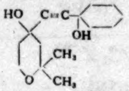


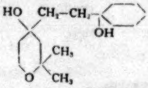
(XX)



(XXI)

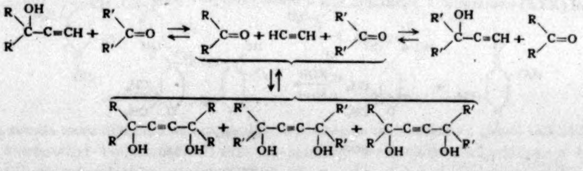
Condensation of the more alkali-resistant pyranol (XVIII) with acetone gives the acetylenic glycol (XIX) in 72.5% yield. Selective hydrogenation of the acetylenic glycol (XIX) with Pd catalyst (1 mole hydrogen) leads to formation of the olefinic glycol (XX), while exhaustive hydrogenation of the acetylenic glycol (XIX) with Ni Catalyst gives the saturated glycol (XXI). On condensation of 2,2-dimethyltetrahydro-4-pyrone (XVII) with ethynylcyclohexanol (VII) under the influence of potassium hydroxide, the acetylenic glycol (XXII) is formed in 23% yield, whereas condensation of the acetylenic pyranol (XVIII) with cyclohexanone gives the acetylenic glycol (XXII) in 41% yield:


(XXII)

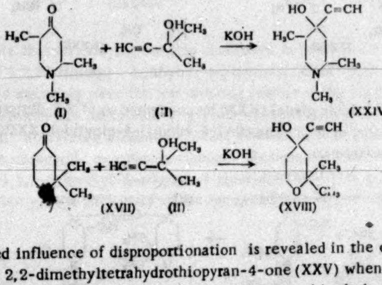

(XXIII)

Exhaustive hydrogenation of the acetylenic glycol (XXII) in presence of Ni catalyst under a low hydrogen pressure (5-10 atm.) leads to formation of the saturated glycol (XXIII).

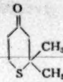
The above-described condensations of acetylenic alcohols (II) and (VII) with the heterocyclic ketones (I) and (XVII) are seriously complicated by simultaneous disproportionation reactions which lead to a mixture of various products:



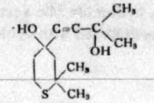
The nature of the equilibrium in these reversible processes is determined by the speed of the oppositely directed reactions of condensation and breakdown, as well as by the stability of the individual components towards caustic alkali. The disproportionation reactions during condensation of 1,2,5-trimethyl-4-piperidone (I) and of 2,2-dimethyltetrahydropyran-4-one (XVII) with dimethylethynylcarbinol (II) leads to formation in about 10% yield of the heterocyclic acetylenic alcohols (XXIV) and (XVIII) side by side with the acetylenic glycols (III) and (XIX):



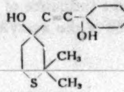
A particularly marked influence of disproportionation is revealed in the condensation of acetylenic alcohols (II) and (VII) with 2,2-dimethyltetrahydrothiopyran-4-one (XXV) when it is impossible to separate the expected heterocyclic acetylenic glycols (XXVI) and (XXVII), and in their place only tetramethylbutynediol (XXVIII) and dihydroxycyclohexylacetylene (XXIX) are obtained:



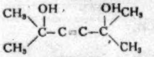
(XXV)



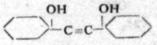
(XXVI)



(XXVII)



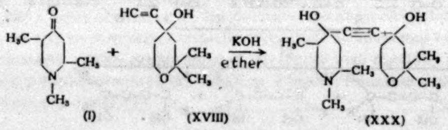
(XXVIII)



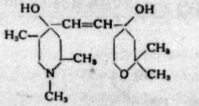
(XXIX)

The acetylenic glycols (XXVI) and (XXVII) with a tetrahydrothiopyran ring could be obtained in a yield of about 40% only by the Grignard-Iotsich method [5] — reaction of 2,2-dimethyltetrahydrothiopyran-4-one (XXV) with magnesium derivatives of the acetylenic alcohols (II) and (VII).

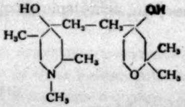
It was of interest also to synthesize unsymmetrical acetylenic γ-glycols whose molecule contain two different heterocycles. Reaction of 1,2,5-trimethyl-4-piperidone (I) with 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol (XVIII) in presence of potassium hydroxide gave a 71% yield of the unsymmetrical heterocyclic acetylenic γ-glycol (XXX) containing a piperidine and a tetrahydropyran ring:



Selective hydrogenation of the acetylenic glycol (XXX) (1 mole hydrogen) in presence of Pd catalyst gave the olefinic glycol (XXXI), while exhaustive hydrogenation with Ni catalyst led to the saturated glycol (XXXII):

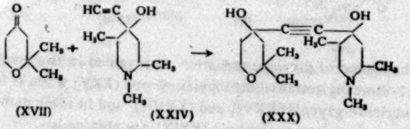


(XXXI)



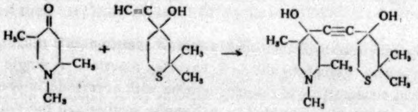
(XXXII)

An attempt to prepare the acetylenic glycol (XXX) by condensation of 2,2-dimethyltetrahydropyran-4-one (XVII) with the α- and β-isomers of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) revealed a difference in the behavior of these geometrical isomers:

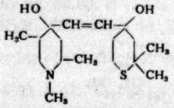


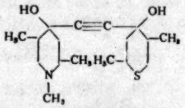
Condensation of ketone (XVII) with the high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) (m.p. 177-178°) gives glycol (XXX) although in lower yield than in the case of condensation of piperidone (I) with pyranol (XVIII). Apart from the glycol (XXX) this reaction also gives 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol (XVIII) whose formation provides confirmation of the disproportionation of the original piperidol (XXIV). On condensation of ketone (XVII) with the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol

(XXIV) (m.p. 110-111°), the only product detected is a viscous substance, rapidly darkening in the air and containing traces of nitrogen. These results show that the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) enters with greater difficulty into condensation with ketones; this behavior is undoubtedly associated with its spatial structure. Condensation of 1,2,5-trimethyl-4-piperidone (I) with 2,2-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII) gave a 46% yield of the acetylenic γ-glycol (XXXIV) which contains a piperidine and a tetrahydrothiopyran ring:

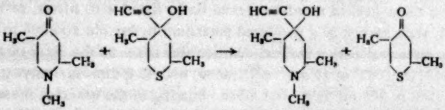

(I) (XXXIII) (XXXIV)

Hydrogenation of the acetylenic glycol (XXXIV) in presence of Pd catalyst goes very slowly and after absorption of 1 mole hydrogen it ceases completely; the ethylenic glycol (XXXV) is formed:

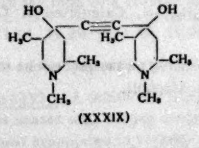

(XXXV)

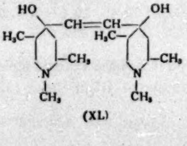

(XXXVI)

Interesting results were obtained on attempting to synthesize the acetylenic glycol (XXXVI) by condensation of 1,2,5-trimethyl-4-piperidone (I) with 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXVII). In place of the expected acetylenic γ-glycol (XXXVI) this reaction gave only disproportionation products, i.e. 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) and 2,5-dimethyltetrahydrothiopyran-4-one (XXXVIII):

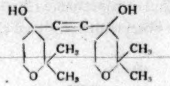

(I) (XXXVII) (XXIV) (XXXVIII)

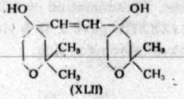
It is interesting to note that on carrying out this condensation in presence of powdered potassium hydroxide, the high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) with m.p. 177-180° was obtained, while condensation in liquid ammonia gave the low-melting isomer of the piperidol (XXIV) with m.p. 110-111°. Synthesis of symmetrical heterocyclic acetylenic γ-glycols was realized by condensation of heterocyclic ketones with appropriate heterocyclic acetylenic alcohols, whereas condensation of heterocyclic ketones with acetylene leads to formation only of heterocyclic acetylenic alcohols. Reaction of 1,2,5-trimethyl-4-piperidone (I) with the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) (m.p. 110-111°) in presence of powdered potassium hydroxide gave a 22% yield of the symmetrical γ-glycol (XXXIX) which contains two piperidine rings:


(XXXIX)

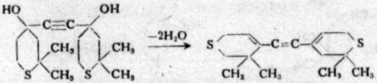

(XL)

Catalytic hydrogenation of the acetylenic glycol (XXXIX) with Pd catalyst goes very slowly; after absorption of 1 mole hydrogen the reaction stops and the ethylenic glycol (XL) is formed. Similarly, the condensation of 2,2-dimethyltetrahydropyran-4-one (XVII) with 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol (XVIII) gave the symmetrical acetylenic γ-glycol (XLI) which contains two tetrahydropyran rings. Selective hydrogenation of this acetylenic glycol with Pd catalyst gave the ethylenic glycol (XLII):


(XLI)


(XLII)

The poor resistance of 2,2-dimethyltetrahydrothiopyran-4-one to caustic alkali makes difficult the synthesis of sulfur-containing acetylenic γ-glycols by the A. E. Favorsky reaction. A single example of the preparation of a glycol of this type by condensation of thiochromanone with acetylene in presence of potassium hydroxide is described in the literature [2a]. We attempted to realize the synthesis of the symmetrical acetylenic γ-glycol (XLIII), which contains two tetrahydrothiopyran rings, by condensation of 2,2-dimethyltetrahydrothiopyran-4-one (XXV) with 2,2-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII) by the Iotsich reaction. It was found, however, that the compound obtained in good yield is not the expected glycol (XLIII) but the product of its dehydration (XLIV):


(XLIII) (XLIV)

We also observed the formation of this product in the synthesis of 2,2-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII) by condensation of 2,2-dimethyltetrahydrothiopyran-4-one (XXV) with acetylene in presence of potassium hydroxide.

EXPERIMENTAL

Acetylenic glycol (III). In a three-necked round-bottomed flask, fitted with stirrer, reflux condenser, thermometer and dropping funnel, were placed 50 g powdered potassium hydroxide and 500 ml anhydrous ether. At a temperature of −4° and with intensive stirring gradual addition was made to the flask of a mixture of 42 g 1,2,5-trimethyl-4-piperidone (I) [7] (b.p. 82° at 12 mm, n_D^{20} 1.4590) and 25 g dimethylethynylcarbinol (II)* (b.p. 103-104°, n_D^{20} 1.4210), dissolved in 300 ml anhydrous ether. Stirring of the reaction mass while cooling the flask with iced water was continued for 9 hours, after which the mass was left overnight. The next day stirring at room temperature was carried out for 5 hours; then at −4° 50 ml water was added and stirring carried out for another ½ hour. The ether layer was separated, the aqueous layer was extracted with ether, and the combined ether extract was neutralized with carbon dioxide and dried with calcined potassium carbonate. After distilling off the ether, the viscous, dark-red product was fractionated in vacuum to give the following fractions: 1) 37-40° at 150 mm; n_D^{20} 1.4212, 4.6 g; 2) 80-84° at 12 mm; n_D^{20} 1.4605, 8.8 g; 3) 105-118° at 3 mm, 5.1 g; 4) 152-154° at 2.5 mm, 40.5 g.

The 1st fraction was the original dimethylethynylcarbinol (II), and the 2nd fraction was the original piperidone (I). Cooling of the 3rd fraction led to separation of 2.4 g high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) [8] with m.p. 176-178°. Redistillation of the 4th fraction gave 36 g pure acetylenic glycol (III) in the form of a non-mobile, vitreous mass with b.p. 148-149° at 2 mm.

Found %: C 69.13, 68.99; H 10.45, 10.57; N 6.23, 6.30. $C_{13}H_{23}O_2N$. Calculated %: C 69.33; H 10.22; N 6.22.

The yield of glycol reckoned on the reacted piperidone was 75.7%; on the piperidone taken it was 60%. The methoiodide of acetylenic glycol (III) melts at 199-201° (from alcohol).

Found %: N 3.45, 3.72. $C_{14}H_{26}O_2NI$. Calculated %: N 3.81.

Acetylenic glycol (VIII). Amounts taken were 84 g powdered potassium hydroxide and 500 ml anhydrous ether; into this mixture was gradually run a mixture of 70 g 1,2,5-trimethyl-4-piperidone (I) and 62 g ethynylcyclohexanol (VII) (b.p. 76-77° at 15 mm, n_D^{20} 1.4805)• in 400 ml anhydrous ether. The reaction was conducted as described above and gave 25 g starting ethynylcyclohexanol (VII) with b.p. 74-79° at 15 mm, 27 g original piperidone (I) with b.p. 44-47° at 3 mm, and 60 g acetylenic glycol (VIII) in the form of a very viscous, vitreous mass with b.p. 170-171° at 1 mm.

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* Prepared by condensation of acetone with acetylene by A. E. Favorsky's method [6].

Found %: C 71.52, 71.73; H 10.07, 10.34; N 5.23, 5.03. $C_{16}H_{27}O_2N$. Calculated %: C 72.40; H 10.25; N 5.27.

The yield on the piperidone reacted was 73%; yield on piperidone taken 45%.

The methiodide of the acetylenic glycol (VIII) melts at 226-228° (from alcohol).

Found %: N 3.57, 3.73. $C_{17}H_{30}O_2NI$. Calculated %: N 3.44.

Ethylenic glycol (IV). 2.5 g acetylenic glycol (III) (b.p. 148-149° at 2 mm) was hydrogenated in a solution of 30 ml alcohol in presence of Pd catalyst on calcium carbonate. In the course of 40 minutes 279 ml hydrogen was absorbed (20°, 742 mm), and hydrogenation was interrupted. The catalyst was filtered off, the alcohol was distilled off, and the viscous, light-yellow residue was distilled in vacuum to give 2.2 g ethylenic glycol (IV) with b.p. 145-146.5 at 2 mm; it partly crystallized. Two recrystallizations from ligroine (b.p. 45-60°) gave 1.1 g ethylenic glycol (IV) with m.p. 155-156°.

Found %: C 69.02, 68.88; H 11.10, 11.14; N 6.32, 6.39; OH 15.23, 14.80 (by the Chugaev-Tserevitinov method). $C_{13}H_{23}(OH)_2N$. Calculated %: C 68.72; H 11.01; N 6.16; OH 14.96.

The hydrochloride of the ethylenic glycol (IV) melts at 171-173° (from alcohol).

Found %: N 5.23, 5.42. $C_{13}H_{26}O_2NCl$. Calculated %: N 5.31.

Saturated glycol (V). 6.8 g acetylenic glycol (III) in 50 ml ethyl alcohol was hydrogenated in presence of Ni catalyst in an autoclave at 8-10 atm. at room temperature. Amount of hydrogen absorbed was 1337 ml compared with 1354 ml required for saturation of the triple bond. The catalyst was filtered off, the alcohol was driven off, and the product was vacuum-distilled. There was obtained 6.4 g saturated glycol (V) in the form of a very viscous liquid, b.p. 141-142° (2 mm).

Found %: C 67.74, 67.70; H 11.90, 12.00; N 6.09, 5.91. $C_{13}H_{27}O_2N$. Calculated %: C 68.07; H 11.87; N 6.10.

Ethylenic glycol (IX). 13.3 g acetylenic glycol (VIII), b.p. 170-171° (1 mm), dissolved in 60 ml anhydrous ethyl alcohol, was hydrogenated in the presence of a Pd catalyst supported in calcium carbonate. In the course of 2 hours 45 minutes 1310 ml hydrogen (28°, 743 mm) was absorbed, and the hydrogenation was interrupted. The catalyst was filtered off, the alcohol was driven off under reduced pressure and the residue in the flask partially solidified. There were obtained 7.5 g acicular crystals with m.p. 147-148° (after two recrystallizations from alcohol) and 5.6 g of a vitreous mass, m.p. 170-171° (2 mm).

Found %: N 5.28, 5.29; OH 12.85, 13.58 (Chugaev-Tserevitinov). $C_{16}H_{27}(OH_2)N$. Calculated %: N 5,24; OH 12.72.

The methiodide of the crystalline ethylenic glycol (IX) has m.p. 270.5° (from alcohol).

Saturated glycol (X). 13.3 g acetylenic glycol (VIII) in 40 ml ethyl alcohol was hydrogenated in the presence of a Ni catalyst in an autoclave under 9-10 atm pressure at room temperature. In the course of 4 hours 2470 ml hydrogen was absorbed compared with 2240 ml required for saturation of the triple bond. The catalyst was filtered off, the alcohol driven off, and the product vacuum-distilled. There was obtained 10.7 g saturated glycol (X) in the form of a vitreous mass, b.p. 172-173° (2 mm).

Found %: C 71.11, 70.85; H 11.46, 11.34. $C_{16}H_{31}O_2N$. Calculated %: C 71.32; H 11.60.

The methiodide of the saturated glycol (X) had m.p. 234° (from alcohol).

Furan derivative (VI). A mixture of 2.3 g saturated glycol (V) (b.p. 141-142° at 2 mm) and 30 ml of 10% sulfuric acid was heated with stirring over a boiling water bath for 4 hours. At the conclusion of the reaction, the solution was evaporated in vacuum and the residue saturated with potassium carbonate and thrice

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• Prepared by condensation of cyclohexanone with acetylene by A. E. Favorsky's method.

extracted with ether. The ethereal extract was dried with calcined potassium carbonate, and after removal of the solvent the residue was distilled in vacuum to give 1.9 g furan derivative (VI) in the form of a mobile yellow liquid with b.p. 101-102° at 6 mm.

n_D^{20} 1.4665, d_4^{20} 0.9229, MR_D 63.48; calc. 63.42.

Found %: C 73.89, 73.76; H 12.02, 11.96; N 6.60, 6.44. $C_{13}H_{25}ON$. Calculated %: C 73.88; H 11.92; N 6.63.

Methiodide of furan compound (VI), (from alcohol) had m.p. 294-295°.

Furan derivative (XI). A mixture of 5.2 g saturated glycol (X) (b.p. 172-173° at 2 mm) in 60 ml 10% sulfuric acid was heated over a boiling water bath with vigorous stirring for 3.5 hours. When the reaction was complete, the solution was steamed down under reduced pressure, the residue was saturated with potash and extracted repeatedly with ether. The ethereal solution was dried over calcined potash and after the ether was driven off, the product was vacuum-distilled. Furan compound (XI) was obtained in the form of a viscous, dark-yellow liquid, b.p. 127-128° at 2 mm.

n_D^{20} 1.4922, d_4^{20} 0.9754, MR_D 74.80; calc. 75.07.

Found %: N 5.36, 5.37. $C_{16}H_{29}ON$. Calculated %: N 5.57.

The methiodide of furan derivative (XI) melts at 272-273° (from alcohol).

Monoacetate (XII). A solution of 8 g acetylenic glycol (III) and 5.6 ml acetyl chloride in 100 ml benzene was heated in presence of 0.9 g metallic magnesium for 6 hours while boiling vigorously. The excess acetyl chloride and benzene were distilled off in vacuum, 50 ml water was run into the residue, the magnesium was filtered off, and the neutral products were extracted from the acid solution. The aqueous solution was then treated with potassium carbonate, the supernatant oily layer was extracted with ether, and after driving off the ether the product was distilled in vacuum to give 6 g of monoacetate (XII) with b.p. 117-118° at 3 mm.

n_D^{20} 1.4710, d_4^{20} 1.001, MR_D 73.98; calc. 74.2.

Found %: C 67.10, 67.10; H 9.44, 9.48; N 5.64, 5.36. $C_{15}H_{25}O_3N$. Calculated %: C 67.38; H 9.43; N 5.24.

Monopropionate (XIII). A mixture of 6.75 g of acetylenic glycol (III), 5.7 ml propionyl chloride, 80 ml anhydrous benzene, and 0.72 g of metallic magnesium was heated for 6 hours with vigorous boiling of the reaction mass. The product was treated the same as above, and we obtained 4 g of the monopropionate (XIII), b.p. 127-128° at 3 mm.

n_D^{20} 1.4695, d_4^{20} 0.9933, MR_D 78.96; calc. 78.94.

Found %: N 4.78, 4.76. $C_{16}H_{27}O_3N$. Calculated %: N 4.97.

Monobenzoate (XIV). A mixture of 6.75 g acetylenic glycol (III), 7.6 ml benzoyl chloride, and 100 ml of anhydrous benzene in the presence of 0.72 g of metallic magnesium was heated with vigorous boiling for 7 hours. After the usual treatment and distillation of the ether, the residue solidified. We obtained 4.2 g of the monobenzoate (XIV), m.p. 160-160.5° (from anhydrous benzene).

Found %: C 72.90, 72.98; H 8.24, 8.32; N 4.58, 4.48. $C_{20}H_{27}O_3N$. Calculated %: C 72.92; H 8.26; N 4.25.

p-Nitrobenzoate (XV). A mixture of 6.75 g acetylenic glycol (III), 12.2 g p-nitrobenzoyl chloride, and 160 ml anhydrous benzene was heated in the presence of 0.72 g metallic magnesium with vigorous boiling of the reaction mixture. The product was treated as described for the monoacetate (XII) synthesis. After the ether was driven off, the residue partially solidified. There was obtained 1.35 g p-nitrobenzoate (XV) with m.p. 188° (from anhydrous alcohol).

Found %: N 7.20, 7.42. $C_{20}H_{26}O_5N_2$. Calculated %: N 7.48.

The hydrochloride of the p-nitrobenzoate (XV) melts at 160-161°.

Found %: Cl 8.90, 8.75. $C_{20}H_{27}O_5N_2Cl$. Calculated %: Cl 8.63.

Monobenzoate (XVI). A mixture of 8.5 g of acetylenic glycol (VIII), 8.9 ml benzoyl chloride and 100 ml anhydrous benzene was heated in the presence of 0.77 g metallic magnesium for 5 hours with boiling of the reaction mass. Crystals appeared at the bottom of the flask towards the end of the heating. The product was worked up as described above. After distillation of the ether the residue partly crystallized. There was obtained 4.8 g benzoate (XVI) with m.p. 158° (from ligroine).

Found %: C 74.38, 74.61; H 8.57, 8.16; N 4.03, 3.74. $C_{23}H_{31}O_3N$. Calculated %: C 74.76; H 8.45; N 3.79.

Acetylenic glycol (XIX). a) In a three-necked flask, fitted with stirrer, reflux condenser, thermometer and dropping funnel, were placed 50.4 g powdered potassium hydroxide and 500 ml anhydrous ether. At a temperature of −4° and with continuous stirring, addition was made of a mixture of 25.2 g dimethylethynylcarbinol (II) and 38.5 g 2,2-dimethyltetrahydropyran-4-one (XVII) [9] (b.p. 174-176°, n_D^{20} 1.4470) in 250 ml anhydrous ether. Stirring while cooling with iced water was continued for 10 hours, after which the reaction mass was left overnight. The next day stirring was carried out at room temperature for another 5 hours. Then with iced water cooling and stirring, 100 ml water was introduced; the aqueous layer was saturated with potassium carbonate and extracted many times with ether. The combined ethereal solution was neutralized with sulfuric acid (1: 2), washed with water and dried with sodium sulfate. After driving off the ether, the viscous residue was distilled in vacuum to give 13.8 g original pyranone (XVII) (b.p. 52-60° at 14 mm, n_D^{20} 1.4492), 6.3 g 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol [1 a] (XVIII) (b.p. 77° at 3 mm, m.p. 87°) and 19.8 g acetylenic glycol (XIX) in the form of a viscous, yellow liquid with b.p. 130-134° at 3 mm.

Found %: C 68.15, 68.18; H 9.34, 9.37; OH 16.47, 16.81 (Chugaev-Tserevitinov). $C_{12}H_{18}(OH)_2O$. Calculated %: C 67.89; H 9.50; OH 16.02.

b) To 8.4 g and 75 ml anhydrous ether, in the course of 10 minutes was added 7.7 g 2,2-dimethyl-2-ethynyltetrahydropyran-4-ol (XVIII) in 100 ml anhydrous ether. Addition was then made in the course of an hour of 5.8 g dry acetone in 25 ml anhydrous ether, and stirring continued for 4 hours. The next day stirring was carried out at room temperature for 7 hours, after which the reaction mixture was left overnight. Hydrolysis and separation of the product were effected as described above. There was obtained 1.9 g original pyranol (XVIII) (b.p. 74-78°, 2.5 mm) and 7.7 g acetylenic glycol (XIX), b.p. 128-132°, 2.5 mm.

Olefinic glycol (XX). 10.6 g acetylenic glycol (XIX), b.p. 130-134° at 3 mm, in 55 ml ethyl alcohol was hydrogenated in presence of Pd catalyst for 4 hours. 1270 ml hydrogen was absorbed as against 1254 ml required for hydrogenation of the acetylenic bond to an olefinic bond. The catalyst was filtered off, the alcohol distilled off, and the viscous, light-yellow residue twice distilled in vacuum to give 6.5 g olefinic glycol (XX) with b.p. 117-117.5° at 2 mm.

Found %: C 67.38, 67.18; H 10.46, 10.42. $C_{12}H_{22}O_3$. Calculated %: C 67.25; H 10.35.

Saturated glycol (XXI). 10.6 g acetylenic glycol(XIX) in 75 ml ethyl alcohol was hydrogenated in presence of Ni catalyst in an autoclave at 10 atm and room temperature. The amount of hydrogen absorbed was 2306 ml against 2240 ml required for complete saturation of the triple bond. The catalyst was filtered off, the alcohol was driven off under reduced pressure, and the residue was distilled two times under reduced pressure. Yield 5.4 g of saturated glycol (XXI), b.p. 118° at 2 mm.

Found %: C 66.30, 66.40; H 10.80, 11.24. $C_{12}H_{24}O_3$. Calculated %: C 66.32; H 11.18.

Acetylenic glycol (XXII). a) 140 g powdered potassium hydroxide and 500 ml anhydrous ether were taken; the flask was cooled with iced water and stirred continuously while addition was made in the course of 2 hours of 64.2 g 2,2-dimethyltetrahydropyran-4-one (XVII) and 93.1 g ethynylcyclohexanol (VII) in 500 ml anhydrous ether. Stirring was continued for 6 hours at 0° and three days at room temperature. The product was hydrolyzed with water, the aqueous layer was separated and extracted with ether, and the combined ethereal solution was washed with dilute sulfuric acid (1: 2) and with water and dried with sodium sulfate. After driving off the ether, the viscous residue was distilled in vacuum to give 23.2 g original acetylenic alcohol VII) (b.p. 79-81° at 15 mm), 11.2 g original pyranol (b.p. 56-57° at 12.5 mm), 2.8 g 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol (XVIII) and 75.8 g of a mixture of acetylenic glycols (XXII) and XXIX) with b.p. 135-165° at 3 mm. Two vacuum fractionations of this mixture gave 24 g acetylenic glycol (XXIX) [10] (b.p. 150-152° at 3 mm; m.p. 106-107°) and 24.5 g acetylenic glycol (XXII) (b.p. 165-167° at 3 mm).

Found %: C 72.01, 72.00; H 9.59, 9.62; OH 13.72, 13.93 (Chugaev-Tserevitinov method). $C_{15}H_{22}(OH)_2O$. Calculated %: C 71.40; H 9.59; OH 13.40.

b) To 16.8 g powdered caustic soda and 100 ml anhydrous ether in the course of 10 minutes was added (with intensive stirring and at a temperature of −4°) 19.6 g of cyclohexanone in 30 ml of anhydrous ether. Then in the course of an hour was introduced 15.4 g 2,2-dimethyl-4-ethynyltetrahydropyranol (XVIII) in 100 ml anhydrous ether. The reaction mass was stirred at −4° for a period of 7 hours. The next day, stirring of the reaction mass was continued for 8 hours and the reaction mass was then left standing for 24 hours. Hydrolysis and working up were performed as described above. There was obtained 12.6 g acetylenic glycol (XXIX) with b.p. 152-155° at 3 mm, and 10.4 g acetylenic glycol (XXII) with b.p. 162-165° at 3 mm.

Saturated glycol (XXIII). 5 g acetylenic glycol (XXII) (b.p. 165-167°, 3 mm) was hydrogenated in 35 ml ethyl alcohol in the presence of 1 g Ni catalyst in an autoclave under 5 atm at room temperature. The catalyst was filtered off, the alcohol was driven off, and the product was vacuum-distilled. We obtained 2.3 g of saturated glycol (XXIII), b.p. 150-151° at 2.2 mm.

Found %: C 70.31, 70.32; H 11.04, 11.33. $C_{15}H_{28}O_3$. Calculated %: C 70.27; H 11.01.

Acetylenic glycol (XXVI). a) In a three-necked flask, fitted with stirrer, reflux condenser, dropping funnel and thermometer, were placed 16.8 g of powdered caustic potash and 100 ml of anhydrous ether. At a temperature of −4° and with stirring a mixture of 14.4 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) [11] (b.p. 47-49° at 2 mm, n_D^{22} 1.4918) and 8.4 g dimethylethynylcarbinol (II) in 200 ml anhydrous ether was introduced. Stirring with iced water cooling was continued 10 hours and next day for another 5 hours at room temperature. After working up in the usual manner and driving off the ether, the residue partly crystallized. There was obtained 7.3 g tetramethylbutynediol (XXVIII) [12], m.p. 91-92°, and 10.1 g resinous residue.

b) To ethylmagnesium bromide, prepared from 2.4 g magnesium and 11 g ethyl bromide in 70 ml anhydrous ether, was added 4.2 g dimethylethynylcarbinol (II) in 20 ml anhydrous ether with iced water cooling and intensive stirring, and the reaction mass was heated at the boiling point of the ether for 3 hours. Addition was then made in the course of 20 minutes of 7.2 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) in 25 ml anhydrous ether. Heating at the boiling point of ether was continued 3 hours, after which the reaction mixture was left overnight. The next day the complex was hydrolyzed with 15 ml dilute hydrochloric acid (1:2), the ether layer was separated, and the aqueous layer was saturated with potassium carbonate and repeatedly extracted with ether. The product was dried with sodium sulfate and after distillation of the ether it was distilled in vacuum to give 3.7 g original thiopyranone (XXV) (b.p. 60-62° at 3 mm) and 4.3 g acetylenic glycol (XXVI), b. p. 150-155° 2.5 mm.

Found %: S 13.65, 13.87. $C_{12}H_{20}O_2S$. Calculated %: S 14.10.

Acetylenic glycol (XXVII). a) 16.8 g powdered potassium hydroxide and 100 ml anhydrous ether were taken; at −4° and with stirring, 14.4 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) and 12.4 g ethynylcyclohexanol (VII) were introduced. Stirring at 0° was continued 10 hours, and the product was left overnight. After the usual treatment, 6.4 g acetylenic glycol (XXIX) with m.p. 106-107° was obtained.

b) To the ethylmagnesium bromide obtained from 2.4 g magnesium and 11 g ethyl bromide in 70 ml anhydrous ether was added, with iced water cooling and stirring 6.2 g ethynylcyclohexanol (VII) in 20 ml absolute ether, and the reaction mass was heated at the boiling point of ether for 4 hours. Gradual addition was then made of 7.2 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) in 20 ml anhydrous ether, and heating at the boiling point of ether was continued 3 hours. The next day the product was hydrolyzed and worked up in the usual manner. There was obtained 2.7 g original acetylenic alcohol (VII) (b.p. 83-85° at 15 mm), 3.6 g original thiopyranone (XXV) (b.p. 48-49° at 2 mm) and 5.75 g acetylenic glycol (XXVII) b.p. 164-168° at 2.5 mm.

Found %: C 67.68, 67.47; H 9.04, 9.04; S 11.85, 11.83. $C_{15}H_{24}O_2S$. Calculated %: C 67.12; H 9.01; S 11.95.

Acetylenic glycol(XXX). a) 25.2 g powdered caustic potash and 225 ml anhydrous ether were taken; at −4° and with stirring 21 g 1,2,5-trimethyl-4-piperidone (I) in 60 ml absolute ether was added. Then in the course of 1 ½ hours addition was made of 11.7 g 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol (XVIII) (m.p. 87°) in 75 ml anhydrous ether. The reaction mass was then stirred at −4° for 7 hours. The next day, stirring was continued for 10 hours at room temperature and the reaction mass was again left standing for 24 hours. We obtained 7.5 g of initial piperidone (I) (b.p. 45-59° at 3 mm), 1 g of initial acetylenic alcohol (XVIII) (b.p. 87° at 2.5 mm) and 15.9 g of acetylenic glycol (XXX) (b.p. 175-177° at 2.5 mm) by the usual method. A second distillation yielded 11.6 g of acetylenic glycol (XXX) (b.p. 177° at 2.5 mm).

Found %: C 69.44, 69.55; H 10.03, 10.24; N 4.59, 4.63. $C_{17}H_{29}O_3N$. Calculated %: C 69.11; H 9.89; N 4.75.

The methiodide of acetylenic glycol (XXX) has m.p. 293-295° (from alcohol).

b) Starting substances were 16.8 g powdered potassium hydroxide, 150 ml anhydrous ether, 12.8 g 2,2-dimethyltetrahydropyran-4-one (XVII), and in the course of $^1/_2$ hour addition was made of 5.6 g of the high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol with m.p. 176-177°, dissolved in 50 ml anhydrous ether. The experiment and the working-up were on similar lines to the preceding. There was obtained 2.4 g original pyrone (XVII) (b.p. 62-64°, 11 mm, n_D^{21} 1.4495), 0.3 g 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol XVIII) (m.p. 86-87°) and 3.7 g of the above-described acetylenic glycol (XXX) with b.p. 175-180° at 2.5 mm, whose methiodide melts at 293-295°.

c) A similar experiment was run with the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) (m.p. 110-111°). Distillation gave 50% of the original piperidol and 2 g substance with b.p. 175-183°, containing traces of nitrogen; this product was not further investigated.

Olefinic glycol (XXXI). 3.65 g of acetylenic glycol (XXX) (b.p. 177° at 2.5 mm) was hydrogenated in 30 ml of ethyl alcohol in the presence of a Pd catalyst in the course of 2 hours. There was absorbed 320 ml hydrogen against 321 ml required for hydrogenation of the acetylenic bond to the olefinic bond. The catalyst was filtered off, the alcohol was driven off and the product was vacuum-distilled. Yield 2.25 g of olefinic glycol (XXXI), b.p. 166-167° at 2 mm. The methiodide of the olefinic glycol (XXXI) melts at 320-325° (after two recrystallizations from 1:5 alcohol-water mixture).

Found %: N 3.40, 3.35. $C_{18}H_{34}O_3NI$. Calculated %: N 3.19.

Saturated glycol (XXXII). 3 g of acetylenic glycol (XXX) (b.p. 177° at 2.5 mm) was hydrogenated in 50 ml of anhydrous ethyl alcohol in the presence of 1.2 g Ni catalyst in an autoclave at 5 atm and room temperature in the course of 1 hour. The catalyst was filtered off, the alcohol was driven off, and the viscous residue was distilled under reduced pressure. We obtained 2.5 g of saturated glycol (XXXII) (b.p. 174° at 2.5 mm), the methiodide of which melted at 306-307° (with decomp.).

Found %: C 49.06, 48.87; H 8.09, 8.18; N 3.28, 3.22. $C_{18}H_{36}O_3NI$. Calculated %: C 48.97; H 8.22; N 3.17.

2,2-Dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII). Into a flask, fitted with stirrer, reflux condenser, thermometer, dropping funnel and tube for passing in acetylene, were charged 8.4 g powdered potassium hydroxide and 40 ml anhydrous ether. At −15° and with stirring, the ether was saturated with acetylene in the course of 30 minutes, whereupon addition was made of 14.4 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) in 50 ml anhydrous ether, after which acetylene was passed through for another 5 hours and the product left for 24 hours. The next day the stirring was continued at room temperature for 2 hours, and then the reaction mass was hydrolyzed with 40 ml water. The ether layer was separated and neutralized with 5% hydrochloric acid solution. The aqueous layer was many times extracted with ether. The ether extract was dried with sodium sulfate; after driving off the ether the product was distilled in vacuum: 1st fraction, b.p. 82-83°, at 3 mm, n_D^{20} 1.5242, 6.2 g; 2nd fraction, b.p. 178-180°, at 4 mm, 5.1 g.

The 1st fraction was 2,2-dimethyl-4-ethynyl-tetrahydrothiopyran-4-ol (XXXIII) which crystallized on standing; m.p. 62-63° (from petroleum ether with m.p. 40-80°).

Found %: C 63.61, 63.62; H 8.28, 8.21; S 18.71, 18.49. $C_9H_{14}OS$. Calculated %: C 63.48; H 8.29; S 18.83.

The 2nd fraction crystallized when treated with ethyl alcohol. The thiopyranic dienyne (XLIV) was obtained with m.p. 127-128° (see below).

Acetylenic glycol (XXXIV). In a flask were put 8.4 g powdered potassium hydroxide and 75 ml anhydrous ether, followed, at −4° and with stirring, by 7.1 g 1,2,5-trimethyl-4-piperidone (I) and 4.3 g 2,2-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII) in 25 ml anhydrous ether. Stirring of the reaction mass at −4° was continued for 7 hours. The next day, stirring was continued for 10 hours at room temperature and the reaction mass was set aside for 24 hours. After the usual treatment, we obtained 2.7 g of initial piperidone (b.p. 54° at 11 mm) and 3.6 g of acetylenic glycol (XXXIV), b.p. 177-183° at 3 mm.

Found %: N 4.54, 4.58. $C_{17}H_{29}O_2NS$. Calculated %: N 4.50.

Olefinic glycol (XXXV). 2.7 g acetylenic glycol (XXXIV) (b.p. 177-183° at 3 mm) was hydrogenated in 30 ml of ethyl alcohol in the presence of a Pd catalyst. In the course of 5 hours, 205 ml of hydrogen was absorbed as against 221 ml required for hydrogenation of the acetylenic bond to the olefinic bond. The catalyst was filtered off and the alcohol was driven off in vacuum. After fractionation there was obtained 1.9 g olefinic glycol (XXXV), b.p. 188° at 4.5 mm.

Found %: C 65.05, 65.34; H 9.99, 10.01; S 8.98, 8.63; N 4.64, 4.59. $C_{17}H_{31}O_2NS$. Calculated %: C 65.13; H 9.97; S 10.23; N 4.47.

The dimethiodide of the glycol melts at 158-159°.

Found %: N 2.40, 2.23. $C_{19}H_{37}O_2NSI_2$. Calculated %: N 2.35.

Attempts to synthesize the acetylenic glycol (XXXVI). a) Into a flask were put 8.4 g of powdered caustic potash in 75 ml of ether. At −10° and with intensive stirring were introduced 14.1 g 1,2,5-trimethyl-4-piperidone (I) and 8.5 g of 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXVII) [2a] (b.p. 82° at 3 mm, n_D^{20} 1.5090) in 25 ml anhydrous ether. Stirring while cooling with iced water was continued 15 hours and then 30 hours at room temperature. The usual treatment gave 7.9 g original ketone (b.p. 42.5-43° at 3 mm, $n_D^{21.5}$ 1.4615), 2.7 g 2,5-dimethyltetrahydrothiopyran-4-one (XXXVIII) [13] with b.p. 56-63° at 3.5 mm, which crystallized on standing, m.p. 69-70° (from benzene), and 2.5 g high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV), m.p. 177-178°.

b) 50 ml liquid ammonia was put into a flask and cooled with ice-methanol (−70°) while 1.2 g metallic sodium was introduced in small portions. After the sodium had dissolved, 3.7 g 2,5-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXVII) was added, and stirring continued 2 hours. Then 7 g 1,2,5-trimethyl-4-piperidone (I) was added and stirring at −70° continued 5 hours. The next day 100 ml anhydrous ether was added and stirring at room temperature continued 10 hours. With iced water cooling, 16 ml water was added, the ether layer was separated, and the aqueous layer saturated with potassium carbonate and extracted many times with ether. The combined ethereal solution was neutralized with carbon dioxide and dried with sodium sulfate. After driving off the ether, the residue in the flask partly crystallized. Recrystallization from benzene gave 1.8 g low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) with m.p. 110-111°. The gasoline-insoluble crystals were recrystallized from alcohol. There was isolated 0.1 g high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) with m.p. 176-178°. The viscous liquid remaining after separation of the crystals was distilled in vacuum to give 2 g original ketone (I) (b.p. 42-44° at 2.5 mm), 1.5 g 2,5-dimethyltetrahydropyran-4-one ((XXXVIII) with b.p. 57-62° at 2.5-3 mm, and 3.1 g of a fraction with 88-96° at 2.5 mm, which partly crystallized. From this fraction was obtained 1.1 g low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV), m.p. 110-111°.

Acetylenic glycol (XXXIX). a) In a round-bottomed 3-necked flask, fitted with stirrer, reflux condenser, dropping funnel and tube for passing through acetylene, was put 34 g powdered potassium hydroxide and 100 ml anhydrous ether. The flask was cooled with ice-salt mixture and with vigorous stirring 28.2 g 1,2,5-trimethyl-4-piperidone (I) was introduced; in the course of 3 ½ hours 2.25 liters acetylene was introduced in a slow stream. The reaction mass was stirred 4 hours while cooling with iced water. The next day, while cooling with iced water and stirring, 35 ml water was added; the ether layer was separated from the aqueous layer, and the precipitate was filtered, washed with water and twice recrystallized from alcohol. Yield 2.1 g high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV), m.p. 177-178°. The aqueous layer was saturated with solid potassium hydroxide and extracted with ether. The combined ethereal solution was neutralized with carbon dioxide and dried with sodium sulfate. After driving off the ether the product was distilled in vacuum. There was obtained 1.9 g of initial piperidone (b.p. 69-70° at 8 mm) and 12 g of the fraction with b.p. 95-105°, at 4 mm, from which we isolated 10.3 g of the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV), m.p. 110-111° (after two recrystallizations from water). The residual viscous and black material was dissolved in ether and dry hydrogen chloride was passed into the solution. The dihydrochloride of acetylenic glycol (XXXIX) was obtained with m.p. 290-291° (after many crystallizations from ethyl alcohol).

Found %: N 7.31, 7.21; Cl 18.52. $C_{18}H_{34}O_2N_2Cl_2$. Calculated %: N 7.36; Cl 18.64.

b) Into a flask was put 16.8 g powdered caustic potash and 150 ml anhydrous ether. 14.1 g of 1,2,5-trimethyl-4-piperidone (I) in 25 ml of anhydrous ether was added to the reaction flask at −4° in the course of 10 minutes. Then 8.4 g low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) with m.p. 110-111° was introduced in 70 ml anhydrous ether and stirring of the reaction mass was continued for 7 hours at −4°. The next day stirring was continued 10 hours at room temperature, after which the reaction mass was left for 48 hours. The usual treatment gave 6.3 g original piperidone (I) (b.p. 78-80° at 11 mm) and 4 g resinous residue. The viscous slurry, obtained after salting out of the aqueous portion with solid potassium hydroxide, was thoroughly extracted with methanol, chloroform and acetone. The combined extract was dried with sodium sulfate. After driving off the solvent the product was distilled in vacuum to give 1.9 g initial piperidone (I) (b.p. 37-42° at 4 mm), 1.2 g of the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (XXIV) (m.p. 110-111°, from water) and 2.4 g acetylenic glycol (XXXIX) (b.p. 172-177° at 3 mm) in the form of a viscous vitreous mass.

Found %: N 8.98, 8.95. $C_{18}H_{32}O_2N_2$. Calculated %: N 9.08.

The dimethiodide of acetylenic glycol (XXXIX) melts at 290-291° (from 5:1 alcohol-water mixture).

Found %: C 40.38, 40.23; H 6.68, 6.41; N 4.65, 4.68. $C_{18}H_{38}O_2N_2I_2$. Calculated %: C 40.55; H 6.47; N 4.73.

Olefinic glycol (XL). 1.6 g acetylenic glycol (XXXIX) (b.p. 172-177° at 3 mm) in 17 ml anhydrous ethyl alcohol was hydrogenated in presence of Pd catalyst. 113 ml hydrogen was absorbed against 129 ml required for hydrogenation of the acetylenic bond to an olefinic bond. The catalyst was filtered off, the alcohol distilled off and the residue distilled in vacuum to give 1.2 g olefinic glycol (XL), b.p. 177-180° at 3.5 mm.

Found %: N 8.75, 8.95. $C_{18}H_{34}O_2N_2$. Calculated %: N 9.02.

The dimethiodide of olefinic glycol (XL) melted at 313-317° (with decomp.).

Found %: N 4.54, 4.67. $C_{20}H_{40}O_2N_2I_2$. Calculated %: N 4.71.

Acetylenic glycol (XLI). Into a flask were put 16.8 g powdered caustic potash and 150 ml anhydrous ether. At a temperature of −3° and with stirring was introduced 12.8 g 2,2-dimethyltetrahydropyran-4-one (XVII) in 20 ml anhydrous ether. Addition was then made in the course of 0.5 hour of 15.4 g 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol in 120 ml absolute ether, and stirring was continued 10 hours (iced water cooling). The next day stirring at room temperature was carried out for 11 $^1/_2$ hours. The product was worked up and isolated in a similar manner to glycol (XXIII). Yield 1.7 g original pyrone (b.p. 62-70° at 22 mm), 14.2 g fraction with b.p. 115-130° at 4 mm which was not investigated, and 12.6 g acetylenic glycol (XLI) with b.p. 175-182° at 4 mm (after redistillation b.p. 172-175° at 3 mm).

Found %: C 68.73, 69.01; H 9.40, 9.38; OH 12.27, 12.79 (Chugaev-Tserevitinov method). $C_{16}H_{24}(OH)_2O_2$. Calculated %: C 68.05; H 9.28; OH 12.05.

Olefinic glycol (XLII). 4.2 g acetylenic glycol (XLI) (b.p. 172-175° at 3 mm) was hydrogenated in a solution of 45 ml of ethyl alcohol in the presence of a Pd catalyst. 345 ml hydrogen was absorbed in the course of 50 minutes as against 359 required to hydrogenate the acetylenic bond to the olefinic bond. The catalyst was filtered off, the alcohol was driven off and the product was vacuum-distilled. We obtained 3 g of olefinic glycol (XLII), b.p. 152-154° at 2 mm.

Found %: C 67.54, 67.50; H 10.34, 10.08. $C_{16}H_{28}O_4$. Calculated %: C 67.57; H 9.92.

Attempt to synthesize acetylenic glycol (XLIII). To a Grignard reagent, prepared in the usual manner from 2.4 g magnesium and 11 g ethyl bromide was added, with cooling and continuous stirring, 8.5 g 2,2-dimethyl-4-ethynyltetrahydrothiopyran-4-ol (XXXIII) in 50 ml anhydrous ether, and the reaction mass was heated at the boiling point of ether 4 hours. With intensive stirring and cooling of the flask with iced water, 7.2 g 2,2-dimethyltetrahydrothiopyran-4-one (XXV) in 30 ml anhydrous ether was added. Stirring at the boiling point of ether was continued 12 hours and the next day for another 8 hours. The usual treatment gave 1.8 g original ketone (XXV) (b.p. 60-67° at 3.5 mm), 2.3 g initial alcohol (XXXIII) (b.p. 80-85° at 3.5 mm), and 6.1 g thiopyranic dienyne (XLIV) with b.p. 170-173° at 3 mm; m.p. 127-128°.

Found %: C 69.02, 69.07; H 8.06, 8.11; S 22.97, 23.12. $C_{16}H_{22}S_2$. Calculated %: C 69.00; H 7.96; S 23.03.

SUMMARY

1. Syntheses were carried out of diverse heterocyclic γ-glycols containing one or two piperidine, tetrahydropyran and tetrahydrothiopyran heterocycles.

2. Catalytic hydrogenation of these glycols in presence of Pd and Ni catalysts gave the corresponding olefinic and saturated glycols.

3. Five partial esters of acetylenic glycols containing the piperidine ring were prepared.

4. Cyclization of the saturated glycols (V) and (X), containing a piperidine ring, gave the corresponding tetrahydrofuran compounds (VI) and (XI) with a spiran structure.

5. An attempt to synthesize the acetylenic glycol (XLIII), containing two tetrahydrothiopyran rings, led to formation of the thiopyranic dienyne (XLIV).

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MOLECULAR CHROMATOGRAPHY

IV. RESOLUTION OF MIXTURES OF NITROANILINES

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According to the literature the chromatographic method was first applied to the nitroanilines by Karrer and Nilsen [1] for resolution of a mixture of o-, m- and p-nitroanilines. In a series of researches [2] chromatography was used for purification or separation of simple mixtures of nitroanilines and their homologs. In a recent publication Larson and Harvey [3] reported the quantitative chromatographic resolution of some binary and ternary mixtures of mono- and dinitroanilines, as well as of halogen-substituted mononitroanilines.

In the present communication a method is presented for quantitative chromatographic resolution of artificial mixtures consisting of all the isomeric mono- and dinitroanilines, and also 2,4,6-trinitroaniline, from benzene on aqueous alumina. The purpose of the investigation, apart from development of a method of resolution, was the determination of the order of adsorbability of the nitroanilines and a comparison of this characteristic with the physico-chemical properties of the compounds.

In view of the fact that nitroanilines are adsorbed on oxides of alumina from benzene very much more weakly than nitrophenols and nitrophenylnitramines, a more active and less moist alumina containing 2-3% water was used in the investigation.

The preparation of the adsorbent and the experimental apparatus have been already described [4]. Out of the eight mixtures examined, complete resolution was effected in the majority of cases after only a single chromatographic treatment, and the components were usually separated in good yields.

Table 1 shows the experimentally determined orders of adsorbabilities of the nitroanilines (in order of increasing adsorbability).

TABLE 1

Adsorbability series of nitroanilines

Expt. No.	Order of adsorbability •
1	o- < m < p-NA
2	2,5- < 2,3- < 2,4- < 3,4-DNA
3	2,6- < 2,5- < 3,5- < 2,3- < 2,4- < < 3,4-DNA
4	2,5- DNA < p-NA
5	2,4,6-TNA < p-NA
6	2,4,6-TNA < 2,5- < 2,3-DNA
7	2,6-DNA < 2,4,6-TNA < o-NA < < 2,5-DNA < m-NA < p-NA + + 3,5- < 2,3- < 2,4- < 3,4-DNA
8	p-NA < 3,4-DNA < o-NP

TABLE 2

Adsorbability and dipole moments of isomeric nitroanilines

Name of compound	Order of arrangement in the column (bottom to top)	Dipole moment $\mu \cdot 10^{18}$ [8]
	Mononitroanilines	
o-NA	I	4.22
m-NA	II	5.22
p-NA	III	6.81
	Dinitroanilines	
2,6-DNA	I	1.88
2,5-DNA	II	2.67
3,5-DNA	III	5.91
2,3-DNA	IV	7.3
2,4-DNA	V	6.48
3,4-DNA	VI	8.9

• Here and later the following abbreviations are used: NA, DNA, TNA, NP are, respectively, nitroaniline, dinitroaniline, trinitroaniline and nitrophenol.

It follows from Table 1 that the relative order of distribution in the column does not depend upon the number of components in the mixture. For example, in all the mixtures of nitroanilines 3,4-dinitroaniline is adsorbed more strongly, while 2,6-dinitroaniline is adsorbed more weakly than the other components. In the chromatographic resolution of mixtures of nitrophenols and nitrophenylnitramines, an important factor for the adsorbability on aluminas from benzene and ether is, as already reported [4-6], the acidity of the compounds. For nitroanilines, which are very weak bases, the acid-base interaction between alumina and substances in the mixture cannot play a very important part. In this case the predominating influence on adsorbability is evidently exerted by the polarity of the compounds.

Arnold [7] has drawn attention to the great influence of the dipoles on the order of adsorption of mixtures on a polar medium. He arrived at this conclusion on the basis of data of other workers. However, his conclusion was stated in too general a form for it to be applicable to all cases, since no account was taken of the chemical nature of the compounds or of the nature of the adsorbents or solvents. Regarding Arnold's assertion of the importance of the number of individual dipoles in the molecule, and not of the total dipole moment of the molecule, the results obtained in the present investigation compel us to reject this assertion as erroneous.

On comparing the distribution of compounds in the chromatographic column with the total dipole moments of the molecules (Table 2), we can see that for mixtures of the three mononitroanilines and of the six dinitroanilines, the adsorbability falls with decreasing dipole moment of the molecule.

There is only one anomalous case in this series — 2,3- and 2,4-DNA.

The arrangement in the column of the 10 nitroanilines (3 mono-, 6 di-, and 1 trinitroaniline) also in general points to a dependence of adsorbability on the polarity of the molecules, although there is no complete parallelism in this case (Table 3). The position of 2,5-DNA is especially anomalous.

TABLE 3

Adsorbability and dipole moments of isomeric nitroanilines

Name of compound	Order of arrangement in the column (bottom to top)	Dipole moment $\mu \cdot 10^{18}$ [8]
2,6-DNA	I	1.88
2,4,6-TNA	II	3.25
o-NA	III	4.22
2,5-DNA	IV	2.67
m-NA	V	5.22
p-NA	VI + VII	6.81
3,5-DNA		5.91
2,3-DNA	VIII	7.3
2,4-DNA	IX	6.48
3,4-DNA	X	8.9

It is evident that other factors come into play apart from polarity. The solubility of nitroanilines in benzene appears to be an important factor. Unfortunately data on this are absent from the literature. It should be noted that 2,4,6-TNA, with the largest number of dipoles, is adsorbed more weakly than all the mono- and dinitroanilines with exception of 2,6-DNA. It is possible that the relatively weak adsorbability of 2,6-DNA and 2,4,6-TNA is bound up with the structural and spatial form of these molecules as well as with the presence of strong inner-molecular hydrogen bonds.

In the resolution of the mixture of p-NA, 3,4-DNA and o-NP it was found that o-NP is adsorbed the most strongly.

Bearing in mind that 3,4-DNA is adsorbed more strongly than the other bases investigated, while o-NP is the most weakly adsorbed compound in a series of previously investigated nitrophenols and nitrophenylnitramines [4-6], all the investigated compounds can be arranged in the following order of adsorbability: *

2,6-DNA < 2,4,6-TNA < o-NA < 2,5-DNA < m-NA < p-NA + 3,5- < 2,3- < 2,4- < 3,4-DNA <
< o- < m- < p-NP < 2,4-DNP < p- < o-NPNA < 2,4-DNPNA.

EXPERIMENTAL

The design of the apparatus and preparation of the moist alumina have already been described [4]. In the

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* Abbreviations: DNP is dinitrophenol; NPNA and DNPNA are nitro- and dinitrophenylnitramines.

resolution of mixtures, part of the nitroanilines is washed out of the column into the filtrate, and the compounds are isolated from the latter by distillation of the solvent. The colored zones remaining in the column were extracted with a spatula, and the adsorbed nitroanilines were isolated by shaking the zones with a mixture of water and ether. Such a 3-5-fold treatment ensured nearly complete extraction of the nitroanilines from the adsorbent and their passage into ethereal solution, from which the compounds were isolated by distillation of the ether. The crystals were dried in a vacuum-desiccator over anhydrous alumina and weighed; their melting point was then determined.

All experiments were conducted at a slight excess pressure in the apparatus (20-180 mm mercury column) and at room temperature.

1. Resolution of a mixture of o-, m- and p-nitroanilines. 0.04 g of each of the nitroanilines in 10 ml benzene, column 190 × 12 mm, moisture content of alumina 3.50% (110-115°), washing with 175 ml benzene, excess pressure in apparatus 20 mm, later 50 mm. After washing with benzene the following filtrate fractions were collected (in order of displacement): 1st fraction – colorless, 45 ml, empty; 2nd fraction – orange, 12 ml; 0.0370 (93%) orange crystals with m.p. 68.5-69° isolated, mixed sample with o-NA melts at 69.5-71°; 3rd fraction – intermediate, 6 ml; 0.0108 g (27%) crystals with m.p. 84-96° isolated – mixture of o- and m-NA; 4th fraction – yellow, 25 ml; pale-yellow crystals weighing 0.0312 g (78%), m.p. 110-111°, mixed sample with m-NA melts at 110.5-111.5°; 5th fraction – intermediate, 10 ml; crystals weighing 0.0006 g (not investigated); 6th fraction – greenish-yellow, 75 ml; yellow crystals weight 0.0396 g (99%), m.p. 145.5-146°, mixed sample with p-NA melts at 146.5-147°.

Order of adsorbability: o- < m- < p-NA.

2. Resolution of mixtures of 2,3-, 2,4-, 2,5- and 3,4-dinitroanilines. 1.10 g of each dinitroaniline in 80 ml benzene, column 477 × 12.5 mm, moisture content of alumina 2.00% (110-115°), washing with 460 ml benzene, pressure 150 mm, duration of experiment 12 hours.

Washing of the column with benzene caused a lower orange zone to be eluted into the filtrate (1st fraction). The following demarcated zones remained in the column (bottom to top): colorless, 40 mm (empty); orange, 80 mm (2nd fraction); greenish-yellow, 123 mm (3rd fraction); colorless, 3 mm (empty); bright-yellow, 10 mm (4th fraction). Above these were situated a light-yellow (15 mm) and a dirty-orange (3 mm) zone, which were not investigated further. By the above described method, crystals were isolated: 1st fraction – yellow-orange needles, weight 0.10 g (100%), m.p. 138.5-139°, mixed sample with 2,5-DNA (m.p. 140-141.5°) melted at 140-140.5°; 2nd fraction – bright-orange needles, weight 0.09 g (90%), m.p. 126-126.5°, mixed sample with 2,3-DNA (m.p. 127-128°) melted at 125.5-126°; 3rd fraction – greenish crystals, weight 0.07 g (70%, m.p. 177.5-178°, mixed sample with 2,4-DNA (m.p. 180°) melted at 177-178°; 4th fraction – orange needles, weight 0.10 g (100%), m.p. 155-156°, mixed sample with 3,4-DNA (m.p. 156-157°) melted at 155-156°.

Order of adsorbability: 2,5- < 2,3- < 2,4- < 3,4-DNA.

3. Resolution of mixture of 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, and 3,5-dinitroanilines. 0.03 g 2,6-DNA and 0.10 g each of the remaining five isomers in 130 ml benzene, column 617× 12 mm, adsorbent, as in preceding experiment, washing with 400 ml benzene, duration of experiment 12 hours.

Washing of the column with benzene led to elution into the filtrate of the lower bright-yellow zone (1st fraction) and the second from the bottom orange zone (2nd fraction). In the column remained the following demarcated zones: light-orange, 40 mm (not investigated); colorless, 80 mm (not investigated), yellow, 80 mm (3rd fraction); intermediate (3-4th fraction), yellow-orange, 125 mm (4th fraction); greenish-yellow, 100 mm (5th fraction); intermediate (5-6th fraction); bright-yellow, 93 mm (6th fraction); colorless, 10 mm (not investigated) and 4 narrow (total width 14 mm) zones, ranging from a dirty-yellow to a dirty-brown (not investigated). Crystals were obtained by the usual method: 1st fraction – golden-yellow scales, weight 0.030 g (100%), m.p. 139-139.3°, mixed sample with 2,6-DNA (m.p. 139.5-140°) melted at 139.5-140°; 2nd fraction – small yellow needles, weight 0.10 g (100%), m.p. 138.7-139°, mixed sample with 2,5-DNA melted at 139.5-140°; 3rd fraction – yellow-orange crystals, weight 0.064 g (64%), m.p. 161.5-162°, mixed sample with 3,5-DNA (m.p. 160-161°) melted at 160.7-161°; 3-4th fraction (intermediate) – yellow crystals, weight 0.047 g (47%), m.p. 126-135°, not investigated further; 4th fraction – yellow crystals, weight 0.094 g, m.p. 112-113°; for purification it was twice chromatogrammed on the same adsorbent. There was obtained 0.06 g, m.p. 121.5-122°; again chromatogrammed on adsorbent containing 8.00% moisture. There was obtained 0.05 g (50%) bright-yellow crystals with m.p. 127-127.5°, a mixed sample with 2,3-DNA melted at 127.3-127.5°; 5th fraction – yellow crystals, weight 0.091 g (91%), m.p. 178-178.5°, mixed sample with 2,4-DNA melted at 178.5-179°;

5-6th fraction (intermediate) – yellow crystals, weight 0.016 g (16%), were not investigated; 6th fraction – bright-yellow crystals, weight 0.063 g (63%), m.p. 158-158.5°, mixed sample with 3,4-DNA melted at 157.5-158°.

Order of adsorbability: 2,6- < 2,5- < 3,5- < 2,3- < 2,4- < 3,4-DNA.

4. Resolution of mixture of p-nitroaniline and 2,5-dinitroaniline. 0.03 g of each compound in 15 ml benzene, column 173 × 11 mm, adsorbent, as in experiment 2, washing with 110 ml benzene, pressure 20 mm.

The bottom orange zone was eluted into the filtrate (1st fraction), the top zone, greenish-yellow, remaining in the column, was eluted into the filtrate with ether (2nd fraction). There was obtained: 1st fraction – bright-yellow needles, weight 0.03 g (100%), m.p. 138.5-139°, mixed sample with 2,5-DNA melted at 138.5-139°; 2nd fraction – golden-yellow crystals, weight 0.03 (100%), m.p. 148-148.5°, mixed sample with p-NA melted at 148-148.5°.

Order of adsorbability: 2,5-DNA < p-NA.

5. Resolution of mixture of p-nitroaniline and 2,4,6-trinitroaniline. 0.10 g of each compound in 50 ml benzene, column 157 × 13.5 mm, same adsorbent, washing with 140 ml benzene, pressure 40 mm.

The bottom greenish-yellow zone was eluted into the filtrate (1st fraction), the top greenish-yellow zone was extracted from the column and treated with a mixture of ether and water. Isolated: 1st fraction – yellow crystals, weight 0.097 g (97%), m.p. 192-192.5°, mixed sample with picramide (m.p. 192.5-193.5°) melted at 192.5-192.6°; 2nd fraction – yellow crystals, weight 0.099 g (99%), m.p. 150-150.5°, mixed sample with p-NA melted at 148.5-149°.

Order of adsorbability: 2,4,6-TNA < p-NA.

6. Resolution of mixture of 2,3- and 2,5-dinitroanilines and 2,4,6-trinitroaniline. 0.10 g of each compound in 80 ml of benzene, column 421 × 12.5 mm, adsorbent as in experiment 2, washing with 330 ml benzene, pressure 80 mm.

The bottom greenish-yellow zone was eluted into the filtrate and resolved into two fractions (1st fraction and 1st-2nd intermediate fraction). The following zones remained in the column: bright-orange, 120 mm (2nd fraction,and bright-yellow, 155 mm (3rd fraction), separated by a white 20 mm zone. Crystals were isolated in the usual manner: 1st fraction – yellow-greenish stout needles, weight 0.09 g (90%), with m.p. 192.3-193°, mixed sample with picramide melts at 192.3-193.2°; 1st-2nd fraction (intermediate), weight 0.03 g (30%), m.p. 174.5-179°, evidently picramide mixed with 2,5-DNA; 2nd fraction – yellow-orange needles, weight 0.08 g (80%), m.p. 138.5-139°, mixed sample with 2,5-DNA melted at 138.5-139°; 3rd fraction – yellow-orange needles, weight 0.10 g (100%), m.p. 127-127.5°, mixed sample with 2,3-DNA melted at 127-127.5°.

Order of adsorbability: 2,4,6-TNA < 2,5- < 2,3-DNA.

7. Resolution of mixture of the three mononitroanilines, six dinitroanilines and picramide. 0.03 g 2,6-DNA and 0.1 g each of the nine other compounds in 100 ml benzene, column 710 × 13.5 mm, adsorbent as in experiment 2, washed with 500 ml benzene, pressure 180 mm, duration of experiment 14 hours.

Washing gave the following filtrate fractions (in order of displacement): 1st fraction – from greenish-yellow zone; isolated 0.035 g (116.6%) yellow crystals with m.p. 140-140.5°, mixed sample with 2,6-DNA melts at 140-140.5°; 2nd fraction – from yellow-green zone; isolated 0.05 g (50%) greenish-yellow crystals with m.p. 192.5-193°, mixed test with 2,4,6-TNA melts at 192-192.5°; 3rd fraction – from orange zone; isolated 0.12 g substance with m.p. 69-89°; 4th fraction – from the same zone; isolated 0.03 g substance with m.p. 95-97°; 5th fraction – from same zone; isolated 0.22 g substance with m.p. 93-99°.

In the column remained the following demarcated zones (from bottom to top): 6th fraction – yellow, 55 mm, isolated 0.09 g of substance with m.p. 120-125°; 7th fraction – yellow-orange, 150 mm, isolated 0.19 g of substance with m.p. 91-96°; 7-8th fraction (intermediate), extracted 0.02 g of substance; 8th fraction – greenish-yellow, 120 mm; extracted 0.08 g (80%) a substance with mixed sample with 2,4-DNA melted at 177.8-178.2°; 9th fraction – bright-yellow, 93 mm, extracted 0.09 g (90%) of substance with m.p. 157.5-158°, mixed sample with 3,4-DNA melted at 157-157.5°.

Consequently, after a single chromatograming of a mixture of the 10 nitroanilines, it was possible to isolate in the pure form 2,6-DNA, 2,4,6-TNA, 2,4-DNA and 3,4-DNA.

After two chromatogramings of a mixture of the 3rd and 4th fractions on the same adsorbent it was possible to isolate 0.04 g (40%) o-NA with m.p. 71-72.5° which did not show a melting point depression in admixture with authentic o-NA.

After three chromatogramings of the 5th fraction it was possible to isolate 0.03 g (30%) 2,5-DNA with m.p. 134-135°, a mixed sample with an authentic specimen melts at 137.5-138.5°, and also 0.03 g (30%) impure m-NA*.

After two chromatogramings on the same adsorbent with washing with benzene and a small amount of ether, it was possible to isolate from the 7th fraction 0.02 g (20%) 2,3-DNA with m.p. 126-127°, a mixed sample with an authentic preparation melts at 127-127.5°.

Subsequent attempts to isolate p-NA and 3,5-DNA from the remaining mixtures did not lead to satisfactory results.

On the basis of this and of the preceding experiments the investigated nitroanilines are arranged in the following adsorption series: 2,6-DNA < 2,4,6-TNA < o-NA < 2,5-DNA < m-NA < p-NA + 3,5-DNA < 2,3- < < 2,4- < 3,4-DNA.

8. Resolution of a mixture of p-nitroaniline, 3,4-dinitroaniline and o-nitrophenol. 0.10 g of each compound in 90 ml benzene, column 344 × 12 mm, adsorbent as in experiment 2, washing with 120 ml benzene, 280 ml ether, pressure 80 mm.

Washing of the column gave the following filtrate fractions (in order of displacement): 1st fraction – from greenish-yellow zone, isolated 0.09 g (90%) greenish-yellow needles with m.p. 148-148.3°, mixed sample with p-NA melted at 147.8-148°; 2nd fraction from greenish-yellow zone, isolated 0.09 g (90%) yellow crystals with m.p. 157.6-158°, mixed sample with 3,4-DNA melted at 156.5-157°.

From the bright-yellow zone (3rd fraction) remaining in the column, a compound was extracted by treatment with a mixture of benzene and hydrochloric acid [4]. Isolated 0.07 g (70%) yellow crystals with m.p. 44.5-45°, mixed sample with o-NP melts at 44-44.5°.

Order of adsorbability: p-NA < 3,4-DNA < o-NP.

SUMMARY

1. Chromatographic resolution was effected from benzene on aqueous alumina of seven artificial mixtures of all the isomeric mono- and dinitroanilines and 2,4,6-trinitroaniline, and also of a mixture of p-nitroaniline, 3,4-dinitroaniline and o-nitrophenol.

The orders of adsorbability of these compounds were determined.

2. It was shown that the adsorbability of nitroanilines in chromatographic resolution on aqueous alumina from benzene depends in great measure upon the polarity of their molecules, i.e. the fall (or rise) of adsorbability in the majority of cases is associated with a lowering (increase) of the total dipole moment of the molecule.

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* In a separate experiment on resolution of a mixture of m-NA and 2,5-DNA it was found that m-NA is higher up the column (is adsorbed more strongly) than 2,5-DNA.

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* T. p. = C. B. Translation pagination.

NITRATION OF PHENYLTRIFLUOROMETHYL SULPHIDE

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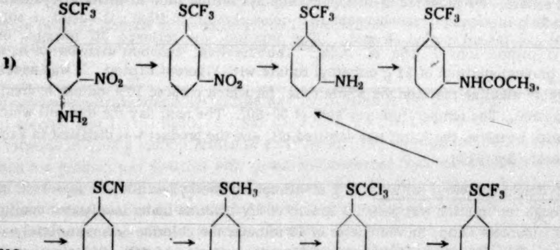
Substitution reactions in the phenyltrifluoromethyl sulfide ring have not previously been studied, and the directive effect of the SCF_3 group has therefore remained unknown. Unlike methylphenyl sulfide, which does not nitrate at low temperatures but is oxidized to methylphenyl sulfoxide [1], phenyltrifluoromethyl sulfide easily forms nitro products.

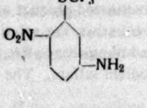
The action on phenyltrifluoromethyl sulfide of nitrating mixture in the cold leads to liquid products of nitration which boil in vacuum in a narrow range. Difficulty was encountered in the separation of these substances by distillation; we therefore reduced the mixture of nitro products to amino compounds and obtained their acetyl derivatives. Separation of this mixture necessitated study of the properties of each isomer individually.

p-Acetylaminophenyltrifluoromethyl sulfide was previously described by one of us and A. I. Kiprianov [2], but the o- and p-isomers were unknown.

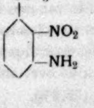
We prepared m-acetylaminophenyltrifluoromethyl sulfide by two routes according to the schemes:



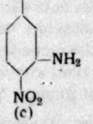
Both methods gave one and the same compound with m.p. 129-130°. o-Acetylaminophenyltrifluoromethyl sulfide could not be obtained from o-nitrothioanisole (similarly to scheme 2) since chlorination of the latter gives o-nitrobenzoylsulfenyl chloride [3]. We chose the following route for preparation of the o-isomer. By nitration of m-acetylaminophenyltrifluoromethyl sulfide followed by removal of the acetyl group with alcoholic alkali, we obtained a mixture of three nitro products:



(a)



(b)



(c)

The mixture of products was distilled with steam; amines (b) and (c) then came over while the non-volatile-in-steam amine (a) was purified by crystallization and then subjected to deamination, reduction and acetylation.

The para-isomer proved considerably less soluble in alcohol than the ortho-isomer. However, although fractional crystallization from alcohol can be employed for separation of the mixture of acetylamino compounds obtained from phenyltrifluoromethyl sulfide, the method is laborious.

We turned our attention to the fact that o-acetylaminophenyltrifluoromethyl sulfide, unlike the para-isomer, readily sublimes on gentle heating; this behavior is evidently due to a formation of a hydrogen bond between the atoms of nitrogen and fluorine. As we found, o-acetylaminobenzotrifluoride also sublimes readily. We easily separated the mixture of acetylamino derivatives by using this method.

The meta-isomer could not be detected in the mixture. In a series of experiments 60-65% para-isomer and 30-35% ortho-isomer were obtained.

We nitrated phenyltrifluoromethyl sulfide also under more drastic conditions – with a mixture of fuming nitric acid and monohydrate at 60°. The resultant mixture of nitro products was reduced with stannous chloride to a mixture of amines which was acetylated. After crystallization the diacetyl derivative of diaminophenyltrifluoromethyl sulfide was isolated. Bearing in mind the ortho- and para-directing effect of the SCF_3 group, it can be assumed that nitration gave 2,4-dinitrophenyltrifluoromethyl sulfide, and that its reduction gave the 2,4-diamine. We obtained the latter in the pure form by saponification of its diacetyl derivative.

From the mixture of acetylamino compounds was also isolated a small amount of p-acetylaminophenyltrifluoromethyl sulfide. Oxidation of m-nitrophenyltrifluoromethyl sulfide with chromic anhydride in sulfuric acid gave m-nitrophenyltrifluoromethyl sulfide. Its reduction with stannous chloride led to m-aminophenyltrifluoromethyl sulfone.

EXPERIMENTAL

m-Nitrophenylmethyl sulfide was prepared by Brand and Leyerzapf [4] from m-nitrothiocyanobenzene by transformation of the latter into 3,3'-dinitrodiphenyl disulfide, which was reduced to 3-nitrothiophenol and methylated with dimethyl sulfate. We prepared m-nitrophenylmethyl sulfide from m-nitrothiocyanobenzene in one step as follows: To 21 g m-nitrothiocyanobenzene in a round-bottomed flask was added a solution of 21 g KOH in 21 ml water and 165 ml methyl alcohol. The mixture was refluxed 30 minutes on a water bath and then was poured into 1 liter of water. The resultant aqueous solution of m-nitrothiophenolate was methylated by gradual addition of 21 g dimethyl sulfate with vigorous stirring. It was necessary that the mixture should have an alkaline reaction the whole time, for which purpose 10% sodium hydroxide solution was added from time to time. The temperature was held at 50-60°. The next day the dark oil which had separated out was extracted with benzene, the latter was distilled off, and the product was distilled in vacuum. B. p. 133-134° at 4 mm. Yield 18 g (91%).

m-Nitrophenyltrichloromethyl sulfide. 18 g m-nitrophenylmethyl sulfide was dissolved in 30 ml dry chloroform and through the solution was passed a stream of dry chlorine under iced water cooling and irradiation with a 200-watt incandescent lamp. In the course of 10 minutes the chlorine was completely absorbed without evolution of hydrogen chloride. Thereafter there was copious evolution of HCl. Chlorination was continued until the required weight increase had been attained; after this the solution was left one hour at room temperature; the chloroform was then distilled off. The product crystallized. Yield 27.3 g (95%). After crystallization from ligroine, it had m.p. 73-74°.

m-Nitrophenyltrifluoromethyl sulfide is mentioned in a patent [5] which gives only its b.p. (103-105° at 10 mm). The preparation was synthesized in the following manner.

a) 27 g m-nitrophenyltrichloromethyl sulfide and 27 g sublimed antimony trifluoride were heated in a Claisen flask over a bare flame until the mixture melted and an exothermic reaction commenced. As soon as the liquid began to distill, the flask was connected to vacuum and the fluorinated product was distilled off together with the antimony trichloride. The mixture was dissolved in 100 ml ether, the solution was washed several times with 6.0 N hydrochloric acid until the wash liquor remained transparent after dilution with water. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. The product was distilled in vacuum. B.p. 113-114° at 20 mm. Yield 17 g (76.6%).

Found %: N 6.11, 6.19. $C_7H_4O_2NSF_3$. Calculated %: N 6.28.

b) 15 g 3-nitro-4-aminophenyltrifluoromethyl sulfide [6] was dissolved in 30 ml alcohol and 8.4 g sulfuric acid (d 1.84) was added; the mixture was cooled to 0° and diazotized with a solution of 4.5 g $NaNO_2$ in 4 ml water. The temperature was held not higher than 10°.

The diazo solution was filtered and refluxed one hour on a water bath. The product was steam-distilled and extracted from the distillate with benzene. The benzene was distilled off and the residue distilled in vacuum. B.p. 113-114° at 20 mm. Yield 10 g (71%).

m-Aminophenyltrifluoromethyl sulfide. 13.6 g m-nitrophenyltrifluoromethyl sulfide was dissolved in 40 ml alcohol, and then gradual addition was made with stirring of a solution of 74 g $SnCl_2 \cdot 2H_2O$ in 50 ml conc. HCl. The mixture was heated one hour on a water bath. The alcohol was distilled off under the vacuum of a water jet pump and the residue was poured on to 300 g ice and 300 ml 40% NaOH. The amine was extracted with ether, the ethereal solution dried over calcined sodium sulfate, the ether distilled off and the amine distilled in vacuum. B.p. 108-110° at 5 mm. Yield 10 g (85%).

Found %: N 6.99, 7.21. $C_7H_6NSF_3$. Calculated %: N 7.25.

The hydrochloride decomposes at 240-241° (in a sealed capillary).

The acetyl derivative melts at 129-130°.

Found %: N 6.07, 6.09. $C_9H_8ONSF_3$. Calculated %: N 5.96.

o-Acetylaminophenyltrifluoromethyl sulfide. 7.5 g m-acetylaminophenyltrifluoromethyl sulfide was put in a three-necked reactor fitted with mechanical stirrer, thermometer and dropping funnel, and slow addition was made (cooling to −5°) of nitrating mixture 12.5 ml HNO_3 (d 1.41) and 41 ml H_2SO_4 (d 1.84). The mass was stirred 2 hours with maintenance of the temperature at 2-4°. The product was poured on ice, filtered, and washed with water. Yield of mixture of isomers of nitro-p-acetylaminophenyltrifluoromethyl sulfide 7.8 g (93%).

The acetyl derivative was saponified by heating the mixture on a water bath with a solution of 2.5 g KOH in 5 ml water and 16 ml alcohol for 15 minutes. After a few hours the solution was diluted with water and the product filtered and washed with water. Yield 6 g (90%).

6 g of the mixture of nitro isomers of m-aminophenyltrifluoromethyl sulfide was steam-distilled. The 3-amino-6-nitrophenyltrifluoromethyl sulfide remaining in the flask was filtered and crystallized from alcohol. Yield 2.2 g, m.p. 126-127°.

2 g 3-amino-6-nitrophenyltrifluoromethyl sulfide was deaminated in the following manner: the amine was dissolved in 5 ml alcohol and 1.3 ml H_2SO_4 (d 1.84) was added; the mass was cooled to 0° and diazotized, with stirring, with a solution of 0.68 g sodium nitrite in 1 ml water. The solution was boiled 2 hours on a water bath, after which the product was distilled with steam and extracted from the distillate with ether; the ethereal solution was dried over Na_2SO_4 and distilled in vacuum. B.p. 78-82° at 8 mm. Yield 1.3 g (65%). Reduction of the prepared o-nitrophenyltrifluoromethyl sulfide to the amine was effected in the usual way by treatment with a hydrochloric acid solution of stannous chloride. The amine was extracted with ether, and after distillation of the ether it was acetylated with acetic anhydride. Yield of o-acetylaminophenytrifluoromethylsulfide 0.8 g; after crystallization from aqueous alcohol it melted at 123-124°. The product readily sublimed. Hydrochloride salt melted at 164-165° (in sealed capillary).

Found %: N 5.9, 6.09. $C_9H_8ONSF_3$. Calculated %: N 5.96.

Nitration of phenyltrifluoromethyl sulfide. a) Nitration with nitrating mixture [HNO_3 (d 1.41) and H_2SO_4 (d 1.84)] in the cold. 20 g phenyltrifluoromethylsulfide was nitrated in a three-necked reactor, fitted with mechanical stirrer, dropping funnel and thermometer, by gradual addition of a nitrating mixture of 22 ml of HNO_3 (d 1.41) and 27 ml of H_2SO_4 (d 1.84) cooled to 0°. The nitrating mixture was added in the course of 20 minutes, and the mixture was then stirred another 3 hours at + 5° and 1 hour at + 15°. The product was poured on ice and extracted with ether. The ethereal extract was washed with water and dried with calcined sodium sulfate; the ether was distilled off and the mixture of o- and p-nitrophenytrifluoromethyl sulfides distilled. Yield 22 g (88%).

For determination of the composition of the mixture of nitro products, the latter was reduced and acetylated in the following way: Into a three-necked reactor, fitted with mechanical stirrer, themometer and dropping funnel, were introduced 160 ml water, 4 ml glacial acetic acid and 25 g iron filings. At the boil and with stirring, gradual addition was then made of 22 g of a mixture of the nitro derivatives of phenyltrifluoromethyl sulfide, after which boiling was continued for 5 hours. The contents of the reactor were made alkaline with sodium carbonate and the product distilled with steam. The distillate was extracted with ether, the ethereal solution dried with calcined Na_2SO_4 and, after removal of the ether, the residue of mixture of amino derivatives of phenyltrifluoromethyl sulfide was distilled in vacuum. B.p. 73-85° at 5 mm. Yield 16 g (84%). 16 g amino compounds was acetylated with 16 ml acetic anhydride. The mixture was diluted with water, heated on a water bath 10 minutes and cooled; the acetylamino compounds were filtered off. Yield 16.5 g (85%).

16 g of the mixture of acetylamino derivatives was sublimed in 3-5 g portions on a watch glass covered with a funnel, while gently heating. From 16 g of the mixture was obtained 5.4 g sublimate with m.p. 123-124° after crystallization from aqueous alcohol. A mixed sample with the above-described o-acetylaminophenyltrifluoromethyl sulfide did not give a depression. Saponification of the acetyl derivative by boiling with 15% hydrochloric acid gave o-aminophenyltrifluoromethyl sulfide with b.p. 70-72° at 7 mm. M.p. 30-31°.

The para-isomer remained unsublimed. Crystallization from 70% aqueous alcohol in presence of carbon gave 9.1 g substance with m.p. 184-185°. No depression in admixture with the pure isomer.

Consequently, resolution of the isomers gave 5.4 g (34%) o-acetylaminophenyltrifluoromethyl sulfide and 9.1 g (57%) p-acetylaminophenyltrifluoromethyl sulfide. The yield of para-isomer is approximately twice that of the ortho-isomer. This ratio was obtained in a series of repeated experiments.

b) Nitration of phenyltrifluoromethyl sulfide with nitrating mixture [HNO_3 (d 1.51) and H_2SO_4 (d 1.84)] at 60°. 10 g phenyltrifluoromethyl sulfide was cooled to −5°, the stirrer was started, and addition of a cooled nitrating mixture of 10.6 g HNO_3 (d 1.51) and 25 g H_2SO_4 (d 1.84) was made in the course of 40 minutes, the temperature being held at not higher than + 5°. The temperature was then gradually raised to 60° and held 20 minutes at this level; the mass was then cooled and poured on ice. The product was extracted with chloroform, the chloroform extract was washed with water to remove acids, the chloroform was driven off, and the residue distilled in vacuum to give two fractions: 1st – to 152° at 12 mm, 1.8 g; 2nd – 156-160° at 12 mm, 10.3 g.

To a solution of 1.8 g nitro compound (1st fraction) in 12 ml alcohol was gradually added a solution of 9.2 g $SnCl_2 \cdot 2H_2O$ in 13 ml concentrated hydrochloric acid, the temperature being held at 60-70°; after that the mixture was heated 40 minutes on a water bath, the alcohol was distilled off, and the residue cooled and poured into a 40% solution of sodium hydroxide containing ice. The amine was extracted with ether, the ethereal extract dried over anhydrous Na_2SO_4, and the ether driven off. The residual amine was acetylated with acetic anhydride. There was obtained 1.2 g mixture of acetyl derivatives. From this mixture could be isolated, by fractional crystallization from alcohol, 0.6 g substance with m.p. 181-182° which did not give a depression in admixture with p-acetylaminophenyltrifluoromethyl sulfide, and 0.4 g with m.p. 223-224°.

A solution of 10.3 g nitro compound (2nd fraction) in 70 ml alcohol was reduced as described above with a solution of 50 g $SnCl_2 \cdot 2H_2O$ in 70 ml concentrated hydrochloric acid. After reduction, the amine was acetylated with 10 ml acetic anhydride. The acetyl derivative was twice crystallized from alcohol. Yield 6.5 g, m.p. 229-230°. Analysis showed that the compound is the diacetyl derivative of diaminophenyltrifluoromethyl sulfide.

Found %: N 9.32, 9.45. $C_{11}H_{11}O_2N_2SF_3$. Calculated %: N 9.58.

The acetyl derivative with m.p. 223-224°, isolated from the 1st fraction, does not give a depression with the substance with m.p. 229-230° and is the same diacetyl derivative.

Thus the reduction and acetylation of the nitro products obtained by nitration of phenyltrifluoromethyl sulfide with fuming nitric acid gave 0.6 g (4.5%) p-acetylaminophenyltrifluoromethyl sulfide and 7 g (41.7%) 2,4-diacetyldiaminophenyltrifluoromethyl sulfide.

2,4-Diaminophenyltrifluoromethyl sulfide. 1 g 2,4-diacetyldiaminophenyltrifluoromethyl sulfide with m.p. 229-230° was refluxed in a small flask with 10 ml 15% hydrochloric acid for 1 hour. After crystallization from aqueous alcohol m.p. 74-75°.

Found %: N 13.41, 13.70. $C_7H_7N_2SF_3$. Calculated %: N 13.46.

m-Nitrophenyltrifluoromethyl sulfone. In a reactor, fitted with mechanical stirrer, thermometer and condenser, were placed 13 g m-nitrophenyltrifluoromethyl sulfide, 8.3 g CrO_3, 8.3 g H_2SO_4 (d 1.84) and 19 ml water. The mixture was stirred 15 hours at 120-130°. The product was steam-distilled and filtered. After crystallization from alcohol it had m.p. 56-57°. Yield 13 g (90%).

Found %: N 5.27, 5.38. $C_7H_4O_4NSF_3$. Calculated %: N 5.49.

The product is referred to in a patent which only gives the b.p. as 146-148° at 11 mm.

m-Aminophenyltrifluoromethyl sulfone. To a solution of 13 g m-nitrophenyltrifluoromethyl sulfone in 35 ml of alcohol was gradually added a solution of 75 g of $SnCl_2 \cdot 2H_2O$ in 55 ml of hydrochloric acid (d 1.19). The temperature was held at 60-70°. The mixture was then heated for one hour over a water bath, the alcohol was driven off and the residue was poured over a mixture of 40% NaOH solution and ice and the product was extracted with benzene. After the benzene was driven off, the amine was crystallized from aqueous alcohol. Yield 8 g (72%, m.p. 78-79°).

Found %: N 6.41, 6.48. $C_7H_6O_2NSF_3$. Calculated %: N 6.22.

SUMMARY

1. o- and m-amino- and acetylaminophenyltrifluoromethyl sulfides were synthesized.

2. It was shown that nitration of phenyltrifluoromethyl sulfide in the cold gives a mixture of o- and p-nitrophenyltrifluoromethyl sulfides; from these were prepared the corresponding amino and acetyl derivatives.

3. The main product of nitration of phenyltrifluoromethyl sulfide at 60° is 2,4-dinitrophenyltrifluoromethyl sulfide. From the latter by reduction and acetylation are obtained 2,4-diamino- and diacetyldiaminophenyltrifluoromethyl sulfides.

4. m-Nitro- and m-aminophenyltrifluoromethyl sulfones are synthesized.

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* T. p. = C. B. Translation pagination.

Found %: S [illegible]. [illegible]. Calculated %: S [illegible].

The product is assumed to be a [illegible] which only [illegible] b.p. at [illegible] at 13 mm.

6. [illegible]. To a mixture of 13.2 g [illegible] in 17 ml of alcohol was gradually added a solution of [illegible]. The temperature was held at [illegible]. The mixture was then heated for one hour over a water bath, [illegible] was given off and the residue [illegible] after the [illegible] was [illegible].

[illegible]

Found %: [illegible]. Calculated %: [illegible].

SUMMARY

1. [illegible] were conducted.

2. It was shown that nitration of [illegible] esters in the cold gives a mixture of o- and p-[illegible], from which the corresponding amino and [illegible] derivatives [illegible].

3. The main product of nitration of [illegible] at 0° is [illegible]. From the latter by reduction and acetylation was obtained [illegible] and [illegible] acids.

4. [illegible] without [illegible].

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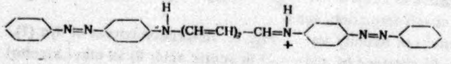
* T. p. = C. B. Translation pagination.

STRUCTURE AND COLOR OF p-PHENYLAZO-SUBSTITUTED ANILS OF GLUTACONIC DIALDEHYDE

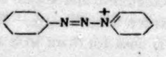
N. E. Grigoryeva and R. M. Zueva

Reaction of 2,4-dinitrophenylpyridinium chloride with p-aminoazobenzene gives [1] the p-phenylazo-substituted dianil of glutaconic dialdehyde;



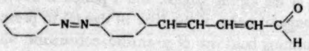
(I)

Cyclization leads to a quaternary salt – p-phenylazophenylpyridinium chloride: :



(II)

and p-aminoazobenzene. This transformation of the dye confirms its structure. p-Phenylazophenylpyridinium chloride is easily cleaved by caustic alkali with formation of the p-phenylazo-substituted monoanil of glutaconic dialdehyde:



(III)

The structure of the monoanil was confirmed by the formation from it of the *dianil* (I).

The symmetrical dye (I) is sparingly soluble in methyl and ethyl alcohols, more soluble in glacial acetic acid. Its concentrated alcoholic solution has a red-violet color similar to that of the corresponding benzidine derivative [2], but unlike the latter the color deepens appreciably on dilution. Depending upon the dilution and the rate of preparation of the solution, various values of the absorption maxima are obtained (525, 500 and 485 mμ). Both (I) and (III) were examined spectroscopically. As we see from Fig. 1, the absorption curves of the dianil (I) in ethyl alcohol (1 and 1') lie in the same region and are similar in character to the absorption curve of the base (2) in ethyl alcohol. The curve 1' was determined after 15 minutes, comparison of these curves shows that the dye changes in course of time.

Fig. 2 contains the absorption curves of dianil (I) in acetic acid and in 96% ethyl alcohol + HCl (in the latter case determinations were made at intervals). The absorption curve in acetic acid is 5 times higher than Curve 2 in alcohol + HCl; the acetic acid solutions of the dye slowly change with time; this process is very rapid in solutions in alcohol + HCl, as can be seen by comparing Curves 2, 2' and 2". Comparison of the absorption curves (Figs. 1 and 2) shows that the dye is hydrolyzed in ethyl alcohol; a salt / base equilibrium is established in the solution; in a neutral solvent this equilibrium is shifted entirely in the direction of formation of the base; hydrochloric acid shifts the equilibrium in the direction of formation of salt. However, the hydrolysis is not complete, as evident from comparison of Curves 2 and 1: in acetic acid the dye is not hydrolyzed and the curve is very strong with a well-marked maximum.

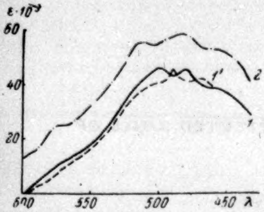


Fig. 1. Absorption curves of dye (I).
1) In ethyl alcohol; 1') in ethyl alcohol after 15 minutes; 2) in presence of caustic alkali.

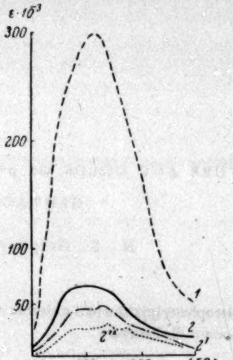


Fig. 2. Absorption curves of dye (I).
1) In acetic acid; 2) in ethyl alcohol + HCl; 2') the same, after 15 minutes; 2'') the same, after 30 minutes.

In order to clarify the influence of acids of different strengths on the character of salt formation, since the base of dye (I) has several centers of basicity we plotted the absorption curves of salts obtained by adding excess of hydrochloric, carbonic and acetic acids to an alcoholic solution of the base. As we see from Fig. 3, salt formation is similar in presence of hydrochloric and acetic acids. The character of the curves shows that in alcoholic solution hydrolysis occurs in presence of both acids. The curve of absorption in presence of carbonic acid is very different; the latter evidently does not react with all the centers of basicity but only with the strongest center, although our data do not permit us to distinguish this center. The characteristic behavior of dye (I) in solutions is undoubtedly associated with the influence of the phenylazo group. Hydrolysis was also observed in other anils of glutaconic aldehyde, especially when substituted in the aromatic rings with electron-accepting groups [3]. It may be suggested that the phenylazo group acts as an electron-accepting substituent with lowering of the basicity of the nitrogens of the amino groups, and a proton is detached if the solvent, for example alcohol, is capable of accepting it. Change of color of the base of dye (I) in presence of acids is undoubtedly associated with the characteristic salt-forming behavior of p-aminoazobenzene which many authors have investigated [4] and is also observed in the unsubstituted anil of glutaconic dialdehyde.

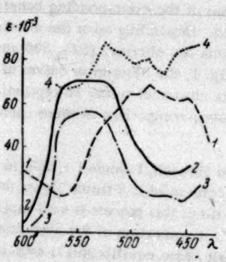


Fig. 3. Absorption curves of the base of dye (I) in ethyl alcohol.
1) Base; 2) base + CH_3COOH; 3) base + HCl; 4) base + H_2CO_3.

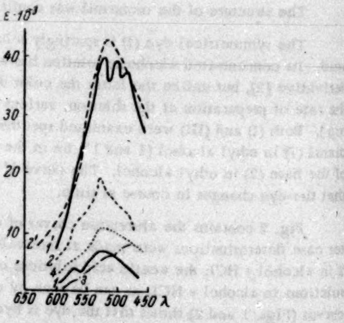
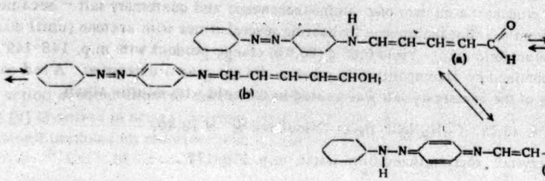
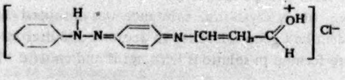


Fig. 4. Absorption curves of dye (III).
1) Acetone + HCl; 1') acetone + NaOH; 2) ethyl alcohol + HCl; 2') ethyl alcohol + NaOH; 3) acetic acid; 4) acetic acid + HCl.

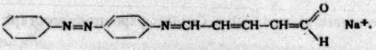
The phenylazo-substituted monoanil of glutaconic dialdehyde (III) in neutral solvents gives relatively stable solutions. This dye belongs to the so-called intrainoid dyes, characteristic of which is the phenomenon of solvatochromy, which has been studied in detail by A. I. Kiprianov and co-workers [5]. The absorption maximum of the monoanil in ethyl alcohol is 465 mμ, in acetone it is 495 mμ; it is an amphoteric base and forms colored salts with acids and alkalies. Its cation and anion have the same color in alcohol (Fig. 4), the absorption maximum is 530 mμ. It may be suggested that in both cases salt formation proceeds at the same centers of basicity, but the considerably greater intensity of the anion demonstrates that the anionoid character of the base is more strongly manifested; the color of the anion is more stable than that of the cation. The structure of the monoanil (III) enables us to postulate the existence of three tautomeric forms:



In presence of acids the formation of Form (c) is more probable:



since it may govern the absorption in the long-wave portion of the spectrum; alkali is bound to shift the equilibrium in the direction of the enol Form (b) with formation of the colored anion:



In acetone solutions in presence of acid and alkali the band splits up and two maxima are formed for the acid salt and three for the anion. The solution of the monoanil (III) in acetic acid has a red color; rapid qualitative determination of the absorption curve gives a maximum at 530 mμ; but this color is unstable and rapidly changes on preparation of a solution of a certain concentration, and non-characteristic Curve 3 is obtained. Addition of hydrochloric acid to the acetic acid solution led to Curve 4, which resembles the absorption curve of the monoanil in acetone + HCl (1).

EXPERIMENTAL

1,5-Bis(p-phenylazophenyleneamino)-pentadien-1,3-ylidene-5-chloride. A mixture of 3 g p-aminoazobenzene and 2.1 g 2,4-dinitrophenylpyridinium chloride in 10 ml ethyl alcohol was heated on a water bath about half an hour. After 3-4 hours the precipitate of dye was filtered off, washed with water, alcohol and ether; after drying it was washed free from dinitroaniline with warm acetone (until disappearance of the red color of the acetone solution with caustic alkali). The so-purified dye formed lustrous green needles (the crystals were perfectly homogeneous under the microscope). Yield 3.4 g (92%). If the condensation is performed in presence of pyridine, the dye is formed after only 3-5 minutes and in a purer form than on condensation in alcohol (yield 84%). For analysis and spectroscopic determinations the dye was twice crystallized from glacial acetic acid or from methyl alcohol (it crystallizes with the solvent). The melting point of the air-dry dye, recrystallized from methyl alcohol, is 138-139°; recrystallized from glacial acetic acid it is 152-153°. After drying 1 hour at 80-90° the melting point rises: from methyl alcohol to 156-158°, from acetic acid to 172-173°.

The dye is soluble in pyridine, acetic acid and methyl and ethyl alcohols, very poorly soluble in water and acetone; it changes color in different solvents.

Found %: N 16.09. $C_{29}H_{25}N_6Cl \cdot CH_3OH$. Calculated %: N 16.02.

p-Phenylazophenylpyridinium chloride was prepared by decomposing the dye in pyridine, water and in the dry form. 1 g dye in 15 ml pyridine was heated until the fuchsine color changed to greenish-brown. The next day an orange, crystalline precipitate came down which was readily soluble in water and alcohol, less soluble in pyridine, and quite insoluble in acetone. The melting point of the product after washing with ether was 148°. Yield 0.5 g (84%). After decomposition of the dye in water at the boil followed by the usual purification [2] the yield of salt was about 60%. Decomposition in the dry form was carried out in 15-20 minutes at 125-128°, the original color disappeared, and the product – a mixture of p-aminoazobenzene and quaternary salt – became orange. The salt was washed free from p-aminoazobenzene by heating several times with acetone (until disappearance of the pink color with hydrochloric acid). Yield 0.65 g (86.6%) orange product with m.p. 148-149°. A mixed sample with the product obtained by decomposition in pyridine did not give a depression. A red color appeared when the aqueous solution of the quaternary salt was treated in the cold with caustic alkali.

Found %: N 13.36, 13.53. $C_{17}H_{14}N_3Cl \cdot H_2O$. Calculated %: N 13.40.

The picrate – bright-orange crystals, recrystallized from water, m.p. 176-177°.

Found %: N 17.33. $C_{23}N_{16}N_6O_7$. Calculated %: N 17.21.

1-(p-Phenylazophenyleneamino)-pentadien-1,3-al-5. To a solution of 0.6 g p-phenylazophenylpyridinium chloride in 5 ml water was added dropwise a 15% solution of sodium hydroxide until precipitate ceased to come down. The precipitate was washed free from caustic alkali with water on the filter and dried. After recrystallization from acetone 0.15 g dark-brown, finely crystalline substance was obtained (under the microscope homogeneous, brown-red crystals). The product had good solubility in acetone and dichloroethane, less so in alcohol and water. Salts with a deeper color are formed in solutions with acids and caustic alkalies.

Found %: N 15.15. $C_{17}H_{15}N_3O$. Calculated %: N 15.16.

The dianil (I) is formed when p-aminoazobenzene and hydrochloric acid are added to the acetic acid solution of the monoanil.

The absorption curves of the dyes were plotted with a Goldberg spectrodensograph.

SUMMARY

1. Two previously undescribed pentamethylene dyes were synthesized: 1) 1,5-Bis-(p-phenylazophenyleneamino)-pentadien-1,3-ylidene-5; 2) 1-(p-phenylazophenyleneamino)-pentadien-1,3-al-5 and the quaternary salt – p-phenylazophenylpyridinium chloride.

2. The absorption curves of the dyes were determined in ethyl alcohol, acetic acid, and ethyl alcohol in presence of NaOH, HCl, CH_3COOH and H_2CO_3, and the causes of the differing absorption of the dyes in different media were examined.

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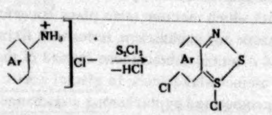
ACTION OF SULFUR CHLORIDE ON β-AMINOANTHRAQUINONE

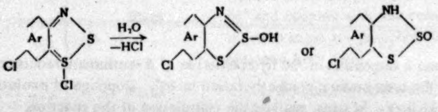
M. K. Bezzubets

The action of sulfur chloride on dry hydrochlorides [1] of aromatic amino compounds or on the free amino compounds [2] dissolved in neutral solvents, with a free para- and one ortho-position in the ring, leads to formation of arylenethiazthionium chlorides with a chlorine atom in the para-position [3]:

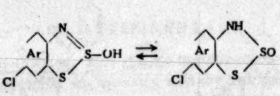


where is an aromatic radical of the benzene or naphthalene series.

Thiazthionium chlorides are unstable [4] and extraordinarily reactive compounds; they readily react with water to form oxygen-containing compounds [5]:



The existence of tautomeric relations between the enolic and the thioketo forms has been proposed for the oxygen-containing arylenethiazthionium compounds [6]:



Oxygen-containing arylenethiazthionium compounds readily react with caustic alkalies with formation of o-aminoarylenemercaptans [7]. This so-called Hertz reaction leads to industrially very important intermediates for sulfur and thioindigo dyes – o-aminoarylenemercaptans [9] and o-aminoarylenethioglycolic acids [10]. A proposed reaction mechanism and the chemical characteristics of the compounds have been reported previously [8].

o-Aminoarylenemercaptans are separated from solutions either in the form of salts of metals [11] or in the form of o-aminoarylenethioglycolic acids, using the quantitative reaction of condensation of mercaptides with a salt of chloroacetic acid [12]. o-Aminoarylenethioglycolic acids readily undergo closure of the lactam ring under the action of inorganic acids. Lactams of o-aminoarylenethioglycolic acids are used for quantitative and qualitative characterization of the course of the Hertz reaction [13].

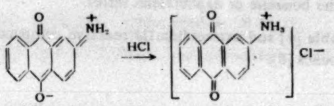
Hydrochlorides of amino compounds are usually employed in the benzene series for preparation of arylenethiazthionium compounds (and the corresponding o-aminoarylenemercaptans) by the Hertz reaction.

Our attempts to use the free amino compounds, dissolved in neutral solvents, were unsuccessful due to the extreme violence of the reaction.

In the naphthalene series the reaction of sulfur chloride with the free amino compounds in solution in neutral solvents proceeds less violently, as shown by Vannotti, and the preparation of naphthylene-thiazthionium chlorides is feasible [6].

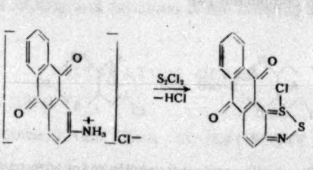
In 1937, in collaboration with V. A. Ignatyuk-Maistrenko an attempt was made to realize the Hertz reaction in the anthraquinone series. The substance chosen for the experiment was β-aminoanthraquinone. Reaction with sulfur chloride took place in glacial acetic acid with gradual raising of the temperature from 20 to 70° in the course of $11\frac{1}{2}$ hours. Under these conditions β-aminoanthraquinone was recovered unchanged. Subsequent experiments were conducted with heating of the mixture of sulfur chloride and β-aminoanthraquinone without a solvent at 100-105° for $11\frac{1}{2}$ hours. The products of the reaction were subjected to aqueous hydrolysis and to alkaline hydrolysis, the latter with simultaneous condensation with the sodium salt of monochloroacetic acid. The isolated and purified compound (dark-green in color) did not give a lactam ring as is characteristic of o-amino-arylenethioglycolic acids (reaction with caustic alkali).

Experiments on the preparation of thiazthionium compounds from β-aminoanthraquinone were subsequently renewed. Bearing in mind the facility with which reaction takes place between sulfur chloride and the hydrochlorides of amino compounds of the benzene and naphthalene series with formation of thiazthionium compounds, it was decided to use the hydrochloride of β-aminoanthraquinone instead of the base. The hydrochloride was obtained by saturating a suspension of β-aminoanthraquinone in glacial acetic acid with dry hydrochloric acid gas. Formation of the hydrochloride is accompanied by thickening and change of color of the β-aminoanthraquinone from reddish-orange to white. The end of the transformation was verified by observation of the mass under the microscope.

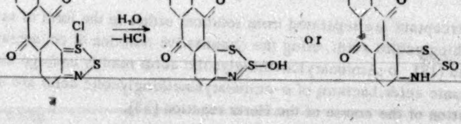


Sulfur chloride was run into a suspension of the hydrochloride of β-aminoanthraquinone in glacial acetic acid at room temperature, and the temperature gradually raised to 80°. Stoppage of evolution of hydrogen chloride, which occurred after 16 hours' heating, marked the completion of the reaction.

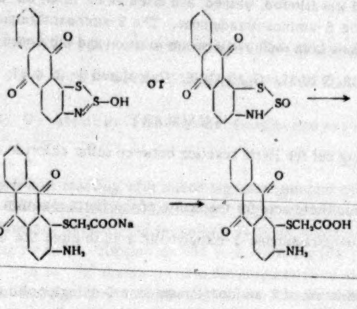
The reaction mass also acquired the brownish-red color which is characteristic of thiazthionium compounds:

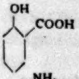
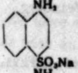
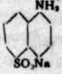
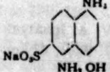
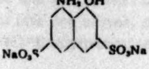


The crystalline mass of brownish-red anthraquinone-2,1-thiazthionium chloride underwent the transformations expected of products of the Hertz reaction, for example reaction with water:



In this reaction the brownish-red color changed to olive, and the aqueous mother liquor showed an acid reaction to congo. Subsequent hydrolysis by caustic soda in presence of sodium monochloroacetate enabled isolation of a brownish-red compound whose content of nitrogen and sulfur corresponded to 2-aminoanthraquinone-1-thioglycolic acid:



Azo components	Color
	Yellow
	Red
	Black
	Black
 . . .	Green

It must be noted that, unlike the o-aminoarylenethioglycolic acids of the benzene and naphthalene series, 2-aminoanthraquinone-1-thioglycolic acid does not close the lactam ring when acidified. Free o-aminoanthraquinonethioglycolic acid readily dissolves in sodium carbonate to form the sodium salt; the acid is regenerated when the sodium salt is treated with inorganic acid. o-Aminoanthraquinonethioglycolic acid was diazotized in presence of hydrochloric acid at 25-30° and coupled with azo components. In the table are set forth some azo components and the color of the dyes obtained from them.

2-Aminoanthraquinone-1-thioglycolic acid did not couple with diazo components; this indicates that the thioglycolic group is in the 1-position of 2-aminoanthraquinone. The Hertz reaction with α-aminoanthraquinone had a course similar to that described above.

EXPERIMENTAL

2,1-Anthraquinonethiazthionium chloride. 22.3 g β-aminoanthraquinone (m.p. 301-302°) was suspended in 150 ml glacial acetic acid. The suspension was saturated with dry hydrogen chloride at room temperature with vigorous stirring. Saturation was continued until formation of β-aminoanthraquinone hydrochloride, as shown by change of the brownish-orange color of the suspension to white. The completion of the transformation was checked by observation under the microscope (disappearance of the brownish-orange crystals). Into the suspension of the hydrochloride of β-aminoanthraquinone at 20° was run 42 g sulfur chloride (b.p. 138°). The mixture was stirred 2 hours and the temperature was gradually raised to 80° and held there for 16 hours until hydrogen chloride ceased to come off. The deep brownish-red reaction mass was filtered and the precipitate washed on the filter with 25 ml glacial acetic acid. Weight of the paste 65 g.

2,1-Anthraquinonethiazthionium oxide. 65 g of the paste of 2,1-anthraquinonethiazthionium chloride was introduced while stirring into a mixture of 600 g ice and 600 ml water. The brownish-red color of the precipitate changed abruptly to olive. After 12 hours the precipitate was filtered (test: on filter paper – colorless blotch, acid reaction to congo) and washed with 500 ml water until the acid reaction disappeared. Weight of moist paste 125 g.

2-Aminoanthraquinone-1-thioglycolic acid. 125 g moist paste of 2,1-anthraquinonethiazthionium oxide was shaken with 10 ml water; about 40 g ice was added to bring the volume to 150 ml and the mass carefully stirred until it had a liquid consistency; addition was then made at +2° of 14 g sodium hydroxide in 100 ml water and 11 g monochloroacetic acid in 20 ml water, neutralized with sodium carbonate. The mixture was stirred at +10° for 2 hours, allowed to stand 12 hours, heated to 70°, diluted with water to a volume of 500 ml and filtered. The filtrate was acidified at 50° with hydrochloric acid until acid to congo. The brownish-red 2-aminoanthraquinone-1-thioglycolic acid was filtered, washed, and dried at 70° in an air-drying cupboard. Weight 16.6 g, yield 51.4% reckoned on the β-aminoanthraquinone. The 2-aminoanthraquinone-1-thioglycolic acid was purified by three reprecipitations from sodium carbonate solution and subjected to analysis.

Found %: N 4.46; S 10.31. $C_{16}H_{11}O_4NS$. Calculated %: N 4.47; S 10.23.

SUMMARY

1. The possibility of carrying out the Hertz reaction between sulfur chloride and β-aminoanthraquinone hydrochloride was demonstrated.

2. The significance of hydrochloric acid for the course of the Hertz reaction was established.

3. The inability of 2-aminoanthraquinone-1-thioglycolic acid to close the lactam ring in an acid medium was established.

4. The possibility of diazotization of 2-aminoanthraquinone-1-thioglycolic acid under the usual conditions was established. In the preparation of azo dyes it can only be used as the diazo component.

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THE REACTION OF PHENYLMAGNESIUM BROMIDE WITH SILICON TETRAFLUORIDE

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Silicon tetrafluoride is capable of reacting with mixed organomagnesium compounds with formation of organosilicon compounds [1]. The usual products are trialkyl- [2] or triarylfluoromonosilanes [3] and only in a few cases has the concomitant formation of tetraalkyl- [1, 2] or tetraarylmonosilanes [4, 5] been observed. Nevertheless, according to A. Ya. Yakubovich and V. A. Ginsburg [6], performance of the reaction in the temperature range of −15 to −70° makes possible the preparation of dialkyldifluoromonosilanes side by side with alkyltrifluoromonosilanes. Reaction between silicon tetrafluoride and α-naphthylmagnesium bromide leads, according to A. D. Petrov and G. I. Chernysheva, to formation of α-naphthylfluoromonosilane and di-α-naphthylfluoromonosilane [7], while tri-α-naphthylfluoromonosilane is also obtained on heating [8].

V. S. Chugunov subjected the products of reaction of silicon tetrafluoride with a 2-fold excess of phenylmagnesium bromide to 4-hours' heating to 100° and obtained tetraphenylmonosilane in a yield of 30% [5].

We have shown that the reaction duration influences the course of the interaction of silicon tetrafluoride with an ethereal solution of phenylmagnesium bromide. It was established that even at a temperature not higher than 0° and with rapid passage of a stream of silicon tetrafluoride into the Grignard reagent, both triphenylfluoromonosilane and diphenyldifluoromonosilane are formed. In addition it was found that triphenylfluoromonosilane is capable of reacting with an etheral solution of phenylmagnesium bromide at room temperature to form tetraphenylmonosilane, although the reaction goes very slowly. On heating for 1 hour to 180-182° and then distilling off the ether, the yield of tetraphenylmonosilane reaches 93%.

It was found that in order to obtain tetraphenylmonosilane in 50% yield directly from silicon tetrafluoride and an ethereal solution of phenylmagnesium bromide, it is advantageous to divide the Grignard reagent into two halves, one of which is treated with silicon tetrafluoride, while the second half is added to the reaction product; the ether is then driven off and the residual product heated to 175-180° for 1 hour.

EXPERIMENTAL

Reaction of phenylmagnesium bromide with silicon tetrafluoride. 1. Into the Grignard reagent, prepared from 70.6 g bromobenzene, 11 g magnesium and 210 ml absolute ether, was passed a strong stream of silicon tetrafluoride for 50 minutes with iced water cooling and constant shaking. The silicon tetrafluoride was obtained by heating a mixture of 24 g sodium fluosilicate, 12 g powdered glass and 30 ml concentrated sulfuric acid in a thick-walled beaker, and it was freed from hydrogen fluoride by passage through a tube containing glass wool. After 24 hours the reaction product, consisting of two liquid layers and crystals, was decomposed, with cooling, by gradual addition of 60 ml 11% hydrochloric acid. The supernatant, yellowish etheral layer was decanted from the aqueous layer and the white precipitate. The aqueous layer and the precipitate were extracted 8 times with ether (660 ml), and the ether from the ethereal solutions was driven off on a water bath. The brownish residue (43.5 g) was then distilled to give a fraction coming over at up to 200° (1.92 g) and containing benzene, bromobenzene and diphenyl. The residual substance (38.1 g) was subjected to numerous fractional distillations in vacuum. The lowest boiling fraction (5.3 g), coming over at 95-161° (28 mm), was redistilled 3 times at atmospheric pressure and gave a colorless liquid (2.73 g) with b.p. 247-248°; it reacted very slowly with water and was identified as diphenyldifluoromonosilane [9].

Found %: F 17.03. $C_{12}H_{10}SiF_2$. Calculated %: F 17.26.

In addition, 2.48 g of less pure diphenyldifluoromonosilane was isolated. A colorless fraction coming over at 30 mm in the temperature range of 245-250° (25.13 g) crystallized on cooling. Recrystallization from ethyl ether gave 18.9 g triphenylfluoromonosilane with m.p. 64°, and 5.9 g less pure product. The total yield of triphenylfluoromonosilane reached 59.5% as compared with 20.9% previously obtained by one of us and N. Z. Kotelkov [3]. The yield of diphenyldifluoromonosilane was 5%.

2. The Grignard reagent, prepared from 33.18 g bromobenzene, 5.14 g magnesium and 98 ml absolute ether, was divided into two equal parts, and in to one of them was passed silicon tetrafluoride (20min.) with shaking and cooling with iced water. The silicon tetrafluoride was obtained by heating 30 g sodium fluosilicate, 15 g glass and 40 ml concentrated sulfuric acid. To the reaction product, consisting of two layers, was added the second half of the Grignard reagent, after which the ether was distilled off on a water bath and, finally, the residual mass was heated 1 hour in an oil bath at 175-180°. With cooling, 20 ml ether was run in and the product then decomposed with 18 ml 16% hydrochloric acid. The ether layer was decanted, 95 ml water was added to the residue, and the whole mass was shaken with 40 ml ether. The ethereal extract was separated, and the crude tetraphenylmonosilane was filtered under reduced pressure and washed with ether (10, 10 and 18 ml) and finally with water (10, 5 and 2 ml). The yield of dried product was 9.1 g (50%), m.p. 223.5-224°. Recrystallization from boiling benzene gave 8.4 g pure tetraphenylmonosilane with m.p. 230.5°.

Reaction of triphenylfluoromonosilane with phenylmagnesium bromide. 1. At room temperature. 4.17 g triphenylfluoromonosilane was dissolved in the Grignard reagent prepared from 4.77 g bromobenzene, 0.75 g magnesium and 17 ml absolute ether. After 2 days, colorless crystals of tetraphenylmonosilane appeared in the flask, and the quantity gradually increased with passage of time. Five days after the start of the experiment, decomposition was effected with 9 ml 9% hydrochloric acid which was added gradually with iced-water cooling and with shaking. The ether layer was decanted, and the residue (3.83 g) was filtered under reduced pressure, washed at first with water (10 ml) and then twice with ether (12 ml). The product remaining on the filter, 0.94 g, had m.p. 226-228°; after recrystallization from boiling benzene it gave 0.85 g pure tetraphenylmonosilane with m.p. 230.5°. From the ethereal solutions was isolated a larger proportion of the original triphenylfluoromonosilane.

2. With heating. The same amounts of components as in the preceding case were taken. The white powder remaining after removal of the ether on a water bath was heated one hour in an oil bath at 180-182°. Into the reaction product, with cooling, was run the recovered ether. The product was then worked up under the conditions described above. The crude tetraphenylmonosilane (5.19 g) was recrystallized from boiling benzene and gave 4.7 g (93%) of pure product with m.p. 230.5°.

SUMMARY

1. It was established that reaction of silicon tetrafluoride with an ethereal solution of phenylmagnesium bromide, even at below 0°, gives diphenyldifluoromonosilane.

2. It was shown that triphenylfluoromonosilane reacts at room temperature with phenylmagnesium bromide with formation of tetraphenylmonosilane.

3. The method of preparing triphenylfluoromonosilane was improved, the yield being increased from 20.9 to 59.5%.

4. It was found that heating of triphenylfluoromonosilane with phenylmagnesium bromide for an hour at 180-182° leads to formation of tetraphenylmonosilane in 93% yield.

5. The method of preparation of tetraphenylmonosilane from Grignard reagent and silicon tetrafluoride, proposed by V. S. Chugunov, was improved and the yield raised to 50%.

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CLEAVAGE OF DIPHENYLCHLOROANTIMONY AND PHENYLDIIODOANTIMONY WITH ACID CHLORIDES AND ALKYL HALIDES IN PRESENCE OF ALUMINUM CHLORIDE

M. S. Malinovsky and S. P. Olifirenko

In a series of papers [1] one of us showed that phenyldichloroarsine, diphenylchloroarsine and some of their substituted derivatives react with acid chlorides in presence of aluminum chloride to give good yields of alkaryl ketones with cleavage of arsenics from the benzene ring.

A similar behavior toward acid chlorides was to be expected in the case of halostibines of the form Ar_2SbX and $ArSbX_2$. We established that diphenylchloroantimony and phenyldichloroantimony react with acid chlorides in presence of anhydrous aluminum chloride and form alkaryl ketones, while the antimony is split off from the benzene ring as antimony halide. Apart from the action of acid chlorides on the halostibines in question, a study was also made of the behavior of the latter toward halogen derivatives of hydrocarbons in presence of aluminum chloride. In this case the formation of alkaryl hydrocarbons was to be expected, and this was also confirmed by experiment.

The yields of ketones and hydrocarbons depend in large measure on the reaction conditions. Prolonged standing of the reaction mixture (at first in iced water and then at room temperature) increases the yield. Lengthy heating on a water bath with the objective of removing the hydrocarbon lowers the yield.

Formation of hydrocarbons from halostibines in presence of aluminum chloride is possible only if antimony is split off in the form of antimony halide from the benzene ring. The presence of released antimony was confirmed by its precipitation with hydrogen sulfide in the form of antimony sulfide. Thus, the breakdown of halostibines under the influence of alkyl halides is represented by the following equations:

$$(C_6H_5)_2SbBr + 2RBr \xrightarrow{AlCl_3} 2C_6H_5R + SbClBr_2 \qquad (1)$$

$$C_6H_5SbI_2 + RBr \xrightarrow{AlCl_3} C_6H_5R + SbBrI_2 \qquad (2)$$

The synthesized compounds and their yields are listed in the table.

Compounds synthesized	Yield (in %)	
	from $(C_6H_5)_2SbCl$	from C_6H_5SbCl
$C_6H_5COCH_3$	52.3	—
$C_6H_5COC_2H_5$	—	75.5
$C_6H_5COCH(CH_3)_2$	63.7	80.0
$C_6H_5COCH_2CH(CH_3)_2$	76.3	84.3
$C_6H_5CH(CH_3)_2$	—	84.2
$C_6H_5CH_2CH_2CH_2CH_3$	44.7 and 68.5	—
$C_6H_5C(CH_3)_3$	46.1	77.8
$C_6H_5CH_2CH_2CH(CH_3)_2$	62.0	60.3

EXPERIMENTAL

For each experiment was taken 7.8 g diphenylantimony (m.p. 68°) which was prepared from diphenylstibine acetate [2]. Cleavage was effected with the calculated amounts of acid chlorides (acetyl, propionyl, isobutyryl and isovaleryl). The aluminum chloride was taken in 1 : 1 ratio to the acid chloride, and the amount of carbon disulfide in each experiment was 80 to 100 g. Reaction was performed by the previously described procedure [1]. After all the acid chloride had been run in, the flask was left in ice and later in water for 20-24 hours. The carbon disulfide was distilled off on a water bath, the residue was decomposed with ice, and the ketone formed was extracted with ether. The ketones were isolated from the ethereal extract (dried with calcium chloride) by vacuum distillation. The ketones were identified from the boiling points, specific gravities, refractive indices, and from the melting points of the semicarbazones. [3].

In an aqueous solution, after extraction with ether, antimony sulfide was precipitated with hydrogen sulfide. The sulfide was filtered, washed, dried, weighed and analyzed. A complete antimony balance was obtained by also determining it in the resinous residue after vacuum distillation of the ketones.

Phenyldiiodoantimony was prepared by the literature method [2]. For each experiment 7.5 g phenyldiiodoantimony was taken. Cleavage was effected by above-described procedure with acid chlorides (propionyl, isobutyryl and isovaleryl), which were taken in amount equivalent to 1 mole acid chloride per phenyl radical of the stibine.

Cleavage of halostibines with halogen derivatives of hydrocarbons in presence of aluminum chloride. Cleavage of diphenylchloroantimony was performed with isobutyl bromide, butyl bromide and isoamyl bromide; phenyldiiodoantimony was cleaved with isopropyl bromide, isobutyl bromide and isoamyl bromide. In each experiment 7.8 g diphenylchloroantimony or 7.5 g phenyldiiodoantimony was taken, together with the calculated amount of alkyl halide. The experiments were run under the conditions described for the acid chlorides. All the hydrocarbons obtained were identified from the boiling points, specific gravities and refractive indices [3].

SUMMARY

1. Diphenylchloroantimony and phenyldiiodoantimony react with acid chlorides in presence of aluminum chloride to form alkaryl ketones.

2. The same halostibines are converted to alkaryl hydrocarbons when treated with alkyl halides in presence of aluminum chloride.

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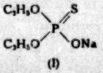
THE REACTIVITY OF THE ALKALI SALTS OF DIALKYLTHIOPHOSPHORIC ACIDS

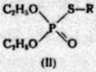
II. ACYLATION REACTIONS

M. I. Kabachnik, T. A. Mastryukova, N. P. Rodionova and E. M. Popov

In the preceding communication we showed [1] that alkali salts of diethylthiophosphoric acid, possessing the thionic structure (I) are alkylated by alkyl halides with migration of the reactive center with formation of S-alkylated derivatives (II):



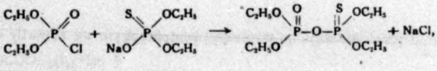
(I)



(II)

Many dually reacting metallic derivatives of tautomeric substances are alkylated and acylated with formation of products of different structure corresponding to the two different tautomeric forms of the original acids. It was consequently of great interest to observe the result of acylation of alkali salts of dialkylthiophosphoric acids.

We did not find any information in the literature on the acylation of alkali dialkylthiophosphates with chlorides of carboxylic acids. Only reactions of these salts with chlorides of acids of phosphorus have been described. Schrader [2], who was the first to report the acylation of sodium diethylthiophosphate with diethyl chlorophosphate, puts forward the following equation for the reaction:

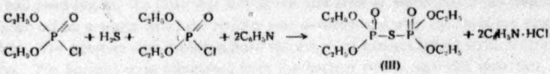


according to which the acylation proceeds at the oxygen.

The constants of the substance obtained agree with the data of A. E. Arbuzov and B. A. Arbuzov [3], who had already prepared it in 1931 by another route which left no doubt about its structure.

According to Schrader the reaction between sodium diethylthiophosphate and diethyl chlorothionphosphate proceeds similarly. Toy [4] synthesized tetraethyldithiopyrophosphate by reaction of diethyl chlorothionphosphate with water in presence of pyridine. He considered the intermediate product of this reaction to be the pyridinium salt of diethylthiophosphoric acid. If this claim is correct, the acylation in this case likewise proceeds at the oxygen.

Fiszer, Michalski and Wieczorkowski [5] arrived at a different conclusion after a study of the acylation of diethyl chlorophosphate; they wrote that reaction goes at the sulfur with formation of a tetraethylthiopyrophosphate with an isomeric structure (III). The thiol structure of the product of acylation is supported by a second method of synthesis discovered by the same authors – reaction of diethyl chlorophosphate with hydrogen sulfide in presence of pyridine:



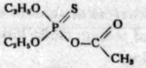
(III)

The constants of the substances got by both methods are identical.

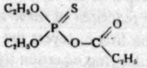
We studied the acylation of the sodium and potassium salts of diethylthiophosphoric acid with acetyl chloride, propionyl chloride and chloroformic esters (methyl and ethyl). The reaction was conducted by adding the acid chloride to the thiophosphate (without solvent) and heat was generated. The physical constants of the compounds obtained are set forth below.

	Formula	Boiling point (pressure in mm)	n_D^{20}	d_4^{20}
1	$(C_2H_5O)_2PSOCOCH_3$	89—90° (4)	1.4553	1.1604
2	$(C_2H_5O)_2PSOCOC_2H_5$	94—94.5 (4)	1.4563	1.1337
3	$(C_2H_5O)_2PSOCOOCH_3$	115—117 (4)	1.4603	1.2181
4	$(C_2H_5O)_2PSOCOOC_2H_5$	114—116(2.5)	1.4560	1.1851

Diethylacetylthionphosphate (IV) has been described in the literature. It was prepared by A. E. Arbuzov and P. I. Alimov by addition of sulfur to diethylacetylphosphite [6]. Schrader also prepared it but did not mention his method. A. E. Arbuzov and P. I. Alimov found for this substance b.p. 93-96° at 3 mm, d_0^{20} 1.1505 and n_D^{20} 1.4511; these data are close to ours although there is no exact agreement. According to Schrader [2] the b.p. is 87° at 1 mm. Since the starting substance for synthesis of diethylacetylthiophosphate (diethylacetylphosphite) is not obtained in the pure form (it cannot be separated from the similtaneously formed diethyl phosphite due to the closeness of their boiling points [6]), we suggested that the discrepancy in the constants may be the consequence of impurity of the preparation; we therefore undertook the synthesis of diethylpropionylthionphosphate (V) by the method of A. E. Arbuzov and P. I. Alimov.

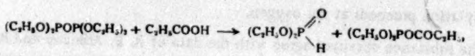


(IV)



(V)

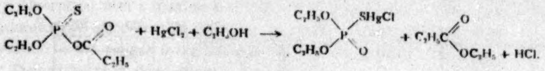
By the action of anhydrous propionic acid on tetraethyl pyrophosphate we actually obtained diethylpropionyl phosphite:



$$(C_2H_5O)_2POP(OC_2H_5)_2 + C_2H_5COOH \longrightarrow (C_2H_5O)_2P(=O)H + (C_2H_5O)_2POCOC_2H_5,$$

which could be separated, although not without difficulty, from traces of diethyl phosphite. Sulfur was added to the product by brief heating to 120°. The so-prepared (yield only 19%) diethylpropionylthionphosphate (V) had the following constants: b.p. 103-105.5° at 5.5 mm, n_D^{20} 1.4514, d_D^{20} 1.1230. These are close to the constants of our acylation product; however, good agreement was not obtained even here. Moreover, the poor yield, the drastic reaction conditions and the relatively unsharp boiling point led us to think that, although both preparations are one and the same substance, the one got by addition of sulfur is impure.

For confirmation of this surmise, we tested the behavior of both preparation towards mercuric chloride in alcoholic solution. Both should react with evolution of 1 equiv. of hydrochloric acid:



However, the preparation got by sulfur addition evolves only 0.87-0.88 equiv. HCl, while the preparation got by acylation evolves 1.02 equiv. This demonstrates the lack of purity of the first preparation.

We therefore made use of the infrared spectra for verification of the structure of the products of acylation of sodium diethyl thiophosphate. In the case of a thiol structure the infrared spectra of the acylation products ought to exhibit an absorption band corresponding to the P = O bond; in the case of a thiono structure the band of the P = S bond should appear.

Gore [7] studied the infrared absorption spectra of a large number of organophosphorus compounds of various types and found that in all cases, when the substances contain the P = O bond the spectrum shows a strong band whose maximum is at 1300-1250 cm^{-1}. This frequency of the P = O bond was previously established by other workers [8] and confirmed by Daasch and Smith [9] who investigated 60 organic compounds of phosphorus.

Thiono compounds only exhibit weak absorption in this region. The spectral characteristic of the P = S bond is somewhat obscure. In many thiophospho organic compounds the absorption band corresponding to the P = S bond, which is liable to large displacements, is weak or is not detected at all. In some compounds the P = S bond is manifested in the infrared spectrum in the form of a strong band in the 650-770 cm^{-1} region. Bellamy and Beecher [10] made a study of p-nitrophenylthiophosphates and found for the P = S bond an absorption band at about 765 cm^{-1}; however, Williams [11] in a study of the infrared spectrum of parathion did not find any characteristic frequencies that might be attributable to the P = S bond.

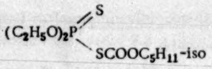
Consequently for establishment of the structure of acyl derivatives of diethylthiophosphoric acid, use should be made of the P = O bond. This was also done by Henglein, Schrader and Mühlman for the spectral analysis of the insecticide "Systox" [12] which likewise did not reveal any absorption bands of the P = S bond.

We studied the infrared spectra in the 3-15 μ region of the following thiono and thiol isomers whose structure we had previously established:

thiono $(C_2H_5O)_2PS(OSH_3)$ [13], $(C_2H_5O)_2PS(OCH_2C_6H_5)$ [1];

thiol $(C_2H_5O)_2PO(SCH_3)$ [13], $(C_2H_5O)_2PO(SCH_2C_6H_5)$ [1];

as well as of



$(C_2H_5O)_2P(=S)SCOOC_5H_{11}\text{-iso}$

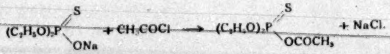
[14] from which the P = O bond is known to be absent. Their spectra are shown in Fig. 1.

As we see from the spectra, the thiol isomers are characterized by a strong absorption band with a maximum at 1255 cm^{-1} (7.97μ), caused by the presence of the P = O bond, whereas the thiono isomers absorb weakly in this region.

Diethylacetylthiophosphate and diethylpropionylthiophosphate do not absorb in the 1300-1250 cm^{-1} region corresponding to the P = O bond. This fact establishes their structure as thiono derivatives.

We also studied the infrared spectra of the original salt – sodium dialkylthiophosphate – in the solid state and in alcoholic solution. In both cases the spectra (Fig. 2) did not contain absorption bands characteristic of the P = O bond, which testifies to the thiono structure of this salt, as was previously found for the potassium salt by Gore [7].

Consequently, since the products of acylation by acetyl chloride and propionyl chloride have a thiono structure, we must assume that acylation of sodium diethylthiophosphate, unlike alkylation [1], goes without transfer of the reaction center:



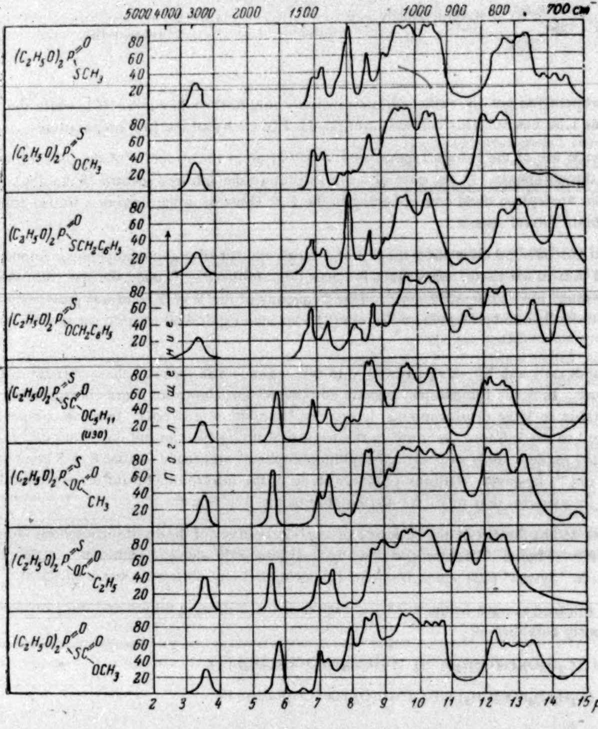


Fig. 1. Infrared spectra of thiophosphoric esters.

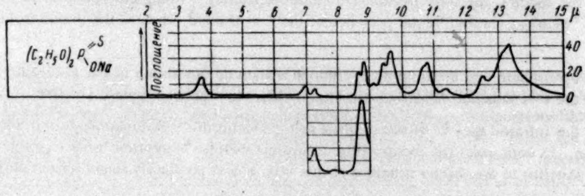


Fig. 2. Infrared spectrum of sodium diethylthiophosphate in the solid state (upper curve) and in alcoholic solution (lower curve).

Concerning diethyl carbomethoxythiophosphate, the investigated preparation shows, quite clearly although not so intensively, absorption with a maximum of 1255 cm^{-1}, which demonstrates the thiol structure. Consequently, acylation with chloroformic ester went at the sulfur, i.e. with transfer of the reaction center. However, the possibility of acylation at the oxygen is not excluded, but the resultant thiono isomer isomerized to the thiol form during distillation (the compound distilled very slowly).

Literature data on the behavior of dialkylacylthionphosphates when heated [15] reveal the possibility of such an isomerization, although it usually requires heating at higher temperatures for a longer period.

EXPERIMENTAL

Acylation of sodium diethylthiophosphate was performed under the same conditions in all cases. To the sodium compound was added a 2- to 3-fold excess of acyl halide; heat was generated and the solid material underwent a marked reduction in bulk. The reaction mixture was then heated on a water bath. On cooling, the precipitated sodium chloride was filtered off, washed with absolute ether and weighed. Its amount was nearly quantitative in all cases. The filtrate was dried over calcined sodium sulfate and fractionated in vacuum. Yield from 20 to 71%.

Diethyl acetylthionphosphate was obtained from 15.6 sodium diethylthiophosphate and 11.8 g acetyl chloride; yield 11.8 g (61%).

B.p. 89-90° at 4 mm, n_D^{20} 1.4553, d_4^{20} 1.1604, MR_D 49.60; calc. 49.40.
Found %: C 33.84, 34.14; H 6.15, 6.39; P 14.42, 14.56. $C_6H_{13}O_4PS$.
Calculated %: C 33.96; H 6.13; P 14.62.

Diethyl propionylthionphosphate was obtained from 15.6 g sodium diethylthiophosphate and 13.9 g propionyl chloride; yield 12.8 g (71%).

B.p. 94-94.5° at 4 mm, n_D^{20} 1.4563, d_4^{20} 1.1337, MR_D 54.27; calc. 54.42.
Found %: C 36.98, 36.91; H 6.61, 6.57; P 13.95, 13.89. $C_7H_{15}O_4PS$.
Calculated %: C 37.16; H 6.68; P 13.70.

Action of alcoholic solution of mercuric chloride on diethyl propionylthionphosphate. To a weighed amount of the substance was added 10 ml 20% solution of mercuric chloride in anhydrous alcohol. A precipitate at once began to come down. After 20 minutes the hydrochloric acid, evolved in the reaction, was back titrated with sodium hydroxide in presence of methyl orange.

0.2442, 0.1796 g sub · 11.60, 8.45 ml, 0.09492N NaOH. Equivalents of HCl found: 1.02, 1.02.

Diethyl carbomethoxythiophosphate was obtained from 19.2 g sodium diethylthiophosphate and 18.9 g methyl chloroformate, yield 9.3 g (43%).

B.p. 115.5-117° at 4 mm, n_D^{20} 1.4603, d_4^{20} 1.2181.
Found %: C 31.27, 31.19; H 6.21, 5.94. $C_6H_{13}O_5PS$. Calculated %:
C 31.58; H 5.75.

Diethyl carbethoxythiophosphate was prepared from 98.4 g of sodium diethylthiophosphate and 27.0 g ethyl chloroformate; yield 10.1 g (21%).

B.p. 114-116° at 2.5 mm (after several distillations in vacuum), n_D^{20} 1.4560, d_4^{20} 1.1851.
Found %: C 35.06, 34.80; H 6.77, 6.54; P 13.05, 12.94. $C_7H_{15}O_5PS$. Calculated %:
C 34.71; H 6.24; P 12.81.

Diethyl propionylphosphite. To 19.5 g tetraethyl pyrophosphite was added dropwise 5.1 g propionic acid. During the addition the temperature rose to 50° in the liquid. At the end of the reaction the contents of the flask were heated to 50° for 5 minutes and then fractionated in vacuum.

B.p. 72.5-74° at 8.5 mm, n_D^{20} 1.4229, d_4^{20} 1.0450, MR_D 47.30; calc. 47.60.
Found %: P 16.15, 16.02. $C_7H_{15}O_4P$. Calculated %: P 15.97.

Preparation of diethyl propionylthionphosphate. 8.86 g diethyl propionylphosphite and 1.28 g sulfur were heated on an oil bath at 107-115° until the whole of the sulfur dissolved. Then, on cooling, the unreacted sulfur was filtered off, and the filtrate was distilled in vacuum. Yield 1.7 g (19%) diethyl propionylthionphosphate.

B.p. 103-105.5° at 5.5 mm, n_D^{20} 1.4514, d_4^{20} 1.1230, MR_D 54.28; calc. 54.42.
Found %: P 14.03, 13.92. $C_7H_{15}O_4PS$. Calculated %: P 13.70.

Action of an alcoholic solution of mercuric chloride. To a weighed amount of substance was added 7 mm of 20% solution of mercuric chloride in anhydrous alcohol. A precipitate at once appeared. After 20 minutes the hydrochloric acid evolved in the reaction was back titrated with sodium hydroxide in presence of methyl orange.

0.1212, 0.1562 g sub.: 8.8, 11.46 ml, 0.05308N NaOH. Found equivalents
HCl = 0.87, 0.88.

The infrared spectra were plotted on a single -ray Perkins Elmer spectrometer (model 12 B) with automatic photorecorder, using a sodium chloride prism. The substance was placed between two plates of rock salt; in all cases the layer thickness was about 0.01 mm.

The salt was obtained in the solid form by evaporating its alcoholic solution on a sylvine plate; the thickness of the layer consequently remained indeterminate. On subsequent plotting of the spectra the character of the spectrum remained unchanged. The concentration of the alcoholic solution of the salt was 0.08 molar; thickness of layer 0.01 mm.

SUMMARY

1. A study was made of the acylation of alkali salts of dialkylthiophosphates with chlorides of carboxylic acids and with esters of chloroformic acid.

2. It was shown that acylation with acetyl chloride and propionyl chloride goes with formation of the corresponding diethyl acetylthionphosphates.

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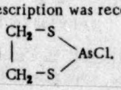
ALKYL- AND DIALKYLARSENIOUS ACID CHLORIDES

Gilm Kamai and Z. L. Khisatova

Unlike the acid chlorides of alkylphosphorous and dialkylphosphorus acids, the chlorides of alkylarsenious and dialkylarsenious acids have been subject of very few investigations. The reason is probably the difficulty of their preparation in the chemically pure state and their susceptibility to hydrolysis.

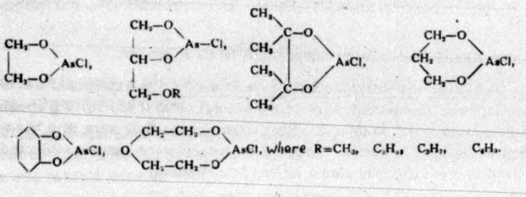
Ethylarsenious chloride (I) and diethylarsenious chloride (II) were first synthesized by McKenzie and Wood [1] by the action of arsenic trichloride on sodium ethoxide:

$C_2H_5OAsCl_2$ (I) $\qquad$ $(C_2H_5O)_2AsCl$ (II)

In a similar manner, i.e. by the action of phenyldichloroarsine on sodium ethoxide, they isolated the acid chloride $C_6H_5AsOC_2H_5Cl$. Classon [2] reacted arsenic trichloride with ethyl mercaptan and obtained the chloride of dithioarsenious acid $(C_2H_5S)_2AsCl$. A description was recently given [3] of the synthesis of the cyclic chloride of ethylenethioglycol arsenious acid .

Kraft [4] pointed out that alcohols do not react with arsenic trichloride either when refluxed in a flask or when heated in a sealed tube, whereas phosphorus trichloride easily enters into reaction with alcohols.

In our laboratory in recent years [5] the reaction of glycols with arsenic trichloride (in presence of anhydrous pyridine) has been applied to the synthesis of a whole series of cyclic chlorides of arsenious acid with the general formulas:



where $R = CH_3, C_2H_5, C_3H_7, C_4H_9$.

We deemed it of interest to repeat the experiments of Kraft and, in addition to establish new methods of preparation of chlorides of alkylarsenious and dialkylarsenious acids.

In a series of experiments we showed that reaction of equimolecular amounts of anhydrous ethyl alcohol and arsenic trichloride leads to good yields (about 70%) of ethoxydichloroarsine (the analog of Menshutkin's acid chloride). When 1 mole each of arsenic trichloride and n-butyl alcohol react together, even with prolonged heating, the reaction between them goes in a complex manner with formation of a series of substances and with evolution of hydrogen chloride. After numerous vacuum distillations in a column, we succeeded in isolating small amounts of butoxydichloroarsine, butoxychloroarsine and tributyl arsenite, the latter in the chemically pure state while the first two were slightly impure. The probable explanation of this transition of butoxychloroarsine to tributyl arsenite is the instability of butoxydichloroarsine and dibutoxychloroarsine at high temperature. This transition may be represented by the following scheme:

$$\text{I.}\quad C_4H_9OH + AsCl_3 \rightleftarrows C_4H_9OAsCl_2 + HCl,$$

$$\text{II.}\quad 2C_4H_9OAsCl_2 \rightleftarrows (C_4H_9O)_2AsCl + AsCl_3,$$

$$\text{III.}\quad 2(C_4H_9O)_2AsCl \rightleftarrows (C_4H_9O)_3As + C_4H_9OAsCl_2,$$

$$\text{IV.}\quad (C_4H_9O)_2AsCl + C_4H_9OAsCl_2 \longrightarrow (C_4H_9O)_3As + AsCl_3.$$

Our reaction of n-butyl alcohol with arsenic trichloride in presence of anhydrous pyridine likewise did not lead to a marked improvement in yield of alkylarsenious acid chlorides.

On reacting equimolecular amounts of tributyl arsenite with acetyl chloride, we synthesized in good yield dibutoxychloroarsine $(C_4H_9O)_2AsCl$. This method can also be used for preparation of other chlorides of dialkylarsenious acids.

In the course of this investigation it appeared of extreme interest to study the reaction of arsenic trichloride with dialkylamines. Experiments on these lines established that reaction of arsenic trichloride with diethylamine in a medium of ethyl alcohol and in a nitrogen atmosphere leads to diethylamino-N-chloroarsine according to the equation:

$$2(C_2H_5)_2NH + AsCl_3 \rightarrow (C_2H_5)_2NAsCl_2 + (C_2H_5)_2NH \cdot HCl.$$

Reaction of 1 mole diethylamino-N-chloroarsine with 2 moles diethylamine under similar conditions gave secondary diethylamino-N-chloroarsine:

$$(C_2H_5)_2N \cdot AsCl_2 + 2(C_2H_5)_2NH \rightarrow [(C_2H_5)_2N]_2AsCl + (C_2H_5)_2NH \cdot HCl.$$

EXPERIMENTAL

Action of arsenic trichloride on ethyl alcohol. In a round-bottomed, 300 ml flask, fitted with reflux condenser connected to a clacium chloride tube, were placed 46.1 g anhydrous ethyl alcohol and 181.3 g freshly distilled arsenic trichloride. On mixing, the temperature of the liquid rose to 51°. Then the mixture was boiled 5 hours in a carbon dioxide stream. The evolved hydrogen chloride was collected in water. The next day the liquid was vacuum-distilled from a flask fitted with a column 50 cm long.

After several distillations 140 g (73%) substance was isolated.

B.p. 58-59° (45 mm), d_4^{20} 1.6762, n_D^{20} 1.5139.
Found %: As 39.30, 39.32; Cl 36.65. $C_2H_5OCl_2As$. Calculated %: As 39.25; Cl 37.15

Monoethylarsenious chloride is a colorless liquid which fumes in the air.

Action of arsenic trichloride on n-butyl alcohol. Experiment 1. The experiment was carried out on similar lines to the preceding one. Components were 74.8 g n-butyl alcohol and 181.3 g arsenic trichloride. The temperature of the liquid rose to 42° on mixing. The contents of the flask were then heated 6 hours. The hydrogen chloride (36.5 g) was trapped in water. The reaction products were likewise subjected to vacuum distillation. The following fractions were obtained after a series of distillations:

1st fraction B.p. 59-63° (2 mm), n_D^{20} 1.5039, d_4^{20} 1.5029.
Found %: As 34.29, 34.45. $C_4H_9OAsCl_2$. Calculated %: As 34.22.

Butoxydichloroarsine is a transparent liquid, easily hydrolyzed by moisture from the air.

2nd fraction B.p. 93° (3 mm), n_D^{20} 1.4680, d_4^{20} 1.2216, MR_D 58.39; calc. 58.11.
Found %: As 29.64, 29.77. $C_8H_{18}O_2ClAs$. Calculated %: As 29.39.

According to the analytical data the isolated substance is dibutylarsenious chloride.

3rd fraction B.p. 109° (4 mm), 49.1 g of product, n_D^{20} 1.4428, d_4^{20} 1.0683.
Found %: As 25.59, 25.57. $C_{12}H_{27}O_3As$. Calculated %: As 25.46.

The final end fraction of numerous distillations is the n-butyl ester of arsenious acid.

Experiment 2. 36.3 g arsenic trichloride was taken in 200 ml absolute ether; with stirring and external cooling a mixture of 14.8 g n-butyl alcohol and 15.8 g anhydrous pyridine in 100 ml absolute ether was gradually run in. The pyridine hydrochloride was later filtered off and washed with ether. The ether was distilled off from this filtrate in a carbon dioxide stream and the residual liquid was vacuum-distilled. By numerous distillations we isolated a small quantity of only one narrow fraction with b.p. 108-109° (4 mm) which is probably tributyl arsenite. We failed to isolate other fractions with narrow boiling ranges.

The impossibility of isolating the acid chlorides in the pure state is evidently associated with gradual change during fractionation from alkoxydichloroarsine to trialkyl arsenite.

Action of acetyl chloride on tributyl arsenite. 20 g n-butyl arsenite and 5.5 g acetyl chloride were heated under reflux for 6 hours on an oil bath.

The reaction products were fractionated. 1st fraction 4.8 g, b.p. 124-125°, n_D^{20} 1.3948, was the acetobutyl ester. The second fraction, 17.1 g, b.p. 110-112° (10 mm), d_4^{20} 1.2116, n_D^{20} 1.4640, MR_D 58.45; calc. 58.11.

Found %: As 29.44, 29.23. $(C_4H_9O)_2AsCl$. Calculated %: As 29.39.

The 2nd fraction – dibutoxychloroarsine – a colorless, light-refracting, easily hydrolyzable liquid.

Action of arsenic trichloride on diethylamine. To 16.1 g diethylamine, dissolved in 500 ml absolute ether, was added dropwise 20 g arsenic trichloride in a nitrogen stream and with external cooling. The precipitated crystals of diethylamine hydrochloride were filtered off, pressed, and washed with ether. The ether was driven off from the filtrate and the residual liquid distilled in vacuum.

There was isolated 22 g (91%) of a fraction with b.p. 83-84° (13 mm), d_4^{20} 1.4727, n_D^{20} 1.5335, MR_D 45.97; calc. 45.16.

Found %: As 34.47, 34.54; Cl 32.75. $C_4H_{10}NCl_2As$. Calculated %: As 34.37; Cl 32.53.

Diethylamino-N-chloroarsine is a colorless, light-refracting, fuming liquid with a faint amine odor. It easily hydrolyzes in the air with formation of a white deposit.

Preparation of secondary diethylamino-N-chloroarsine. Preparation was by the preceding procedure, using 15 g diethylamino-N-chloroarsine and 10.2 g diethylamine in 300 ml ether. Vacuum distillation gave 9.7 g substance.

B.p. 118-120° (17 mm), d_4^{20} 1.2225, n_D^{20} 1.5098. MR_D 62.30; calc. 62.70.
Found %: As 29.69, 29.79. $C_8H_{20}N_2ClAs$. Calculated %: As 29.42.

Secondary diethylamino-N-chloroarsine is a colorless, readily hydrolyzed liquid.

SUMMARY

1. It was shown that reaction of equimolecular amounts of anhydrous ethyl alcohol and arsenic trichloride gives mainly ethoxydichloroarsine.

2. It was established that arsenic trichloride reacts with n-butyl alcohol at elevated temperature in a fairly complex manner with formation of a series of substances, for example n-butoxydichloroarsine, di-n-butoxychloroarsine and tributyl arsenite.

3. It was shown that dibutoxychloroarsine may be obtained in good yield by the action of acetyl chloride on tributyl arsenite.

4. Primary and secondary diethylamino-N-chloroarsines were synthesized for the first time.

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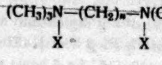
ALKAMINO ESTERS OF SOME HETEROCYCLIC ACIDS AS POSSIBLE HYPOTENSIVE AGENTS

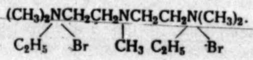
M. V. Rubtsov, E. S. Nikitskaya and V. S. Usovskaya

For the therapy of hypertension, definite interest is attached to substances capable of preventing disturbances in the ganglions of the vegetative nervous system. Few such compounds are known at present; the most active members are bis-quaternary ammonium salts of the composition [1-3]:



$(CH_3)_3N(X){-}(CH_2)_n{-}N(X)(CH_3)_3$

pentamethonium n = 5; hexamethonium n = 6.



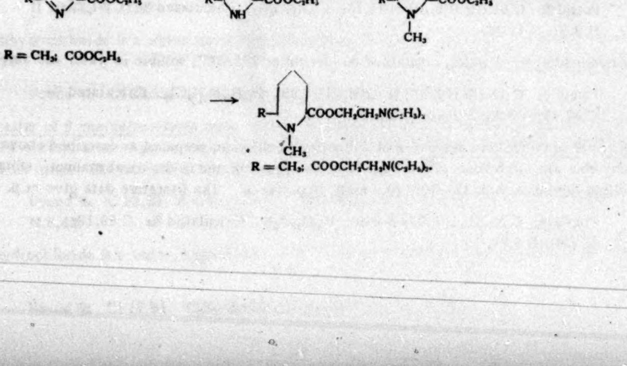
$(CH_3)_2N(C_2H_5)(Br)CH_2CH_2N(CH_3)CH_2CH_2N(C_2H_5)(Br)(CH_3)_2.$

pentamine (pendiamide)

A definite ganglion-blocking action is exhibited by 2,6-dimethyl- and 1,2,6-trimethylpiperidine. Even more active is the ethoiodide of the latter [4]. Considerable activity is also shown by the alkaloids sparteine [5] and pachycarpine [6]. In a series of cases, however, all these substances cause undesirable side effects and are often insufficiently active; further work in this field is therefore extremely important.

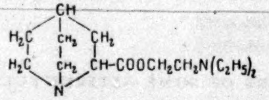
We considered it would be interesting to obtain ganglion-blocking agents in the shape of bis-quaternary salts of alkamino esters of some heterocyclic acids, in particular of pyridine, piperidine and quinuclidine.

2,6-Lutidine served as the starting substance for synthesis of alkamino esters of the pyridine series; it was oxidized with potassium permanganate to dipicolinic [7] and 6-methylpicolinic [8] acids. The latter were transformed, via their chlorides, into the diethylaminoethyl esters. Hydrogenation of the esters with the help of platinum catalyst gave the diethylaminoethyl esters of dipipecolinic and 6-methylpipecolinic acids. We did not succeed in transforming these compounds directly into their N-methyl derivatives; the latter were therefore synthesized according to the following scheme:



The ethyl esters of dipicolinic and 6-methylpicolinic acids were subjected to hydrogenation, followed by methylation and, finally, transesterification.

The diethylaminoethyl ester of α-quinuclidinecarboxylic acid



was obtained by starting from the acid chloride and diethylaminoethanol.

Pharmacological examination of the prepared derivatives, carried out by I. M. Sharapov in the pharmacological laboratory, revealed a high ganglion-blocking action of the dimethiodide of the diethylaminoethyl ester of 1,6-dimethylpipecolinic acid and of the dimethoiodide of the diethylaminoethyl ester of α-quiniclidinecarboxylic acid. In activity they surpass tetraethylammonium iodide by a factor of 15-20.

EXPERIMENTAL

Di-(diethylaminoethyl) ester of dipicolinic acid. A mixture of 3 g dipicolinic acid and 30 ml thionyl chloride was heated at the boil until the acid had dissolved completely (6-8 hours). The resultant dichloride of dipicolinic acid was heated with 30 ml diethylaminoethanol at 110-115° for 6 hours to form the di-(diethylaminoethyl) ester of dipicolinic acid in the amount of 3.6 g (55.4%) in the form of a light-yellow mobile liquid with b.p. 214-215° (0.5 mm), soluble in the common organic solvents and insoluble in water.

Found %: N 11.57. $C_{19}H_{31}O_4N_3$. Calculated %: N 11.50.

The dihydrochloride: a white, crystalline powder, soluble in water and alcohol, m.p. 190-191°.

Found %: N 9.34; Cl 16.79. $C_{19}H_{33}O_4N_3Cl_2$. Calculated %: N 9.58; Cl 16.66.

The dimethiodide: a white, crystalline powder, soluble in water and alcohol, m.p. 200-202°.

Found %: C 38.74; H 5.96; N 6.40; I 39.41. $C_{21}H_{37}O_4N_3I_2$. Calculated %: C 38.82; H 5.70; N 6.47; I 39.13.

Di-(diethylaminoethyl) ester of dipipecolinic acid. A solution of 10.7 g di-(diethylaminoethyl) ester of dipicolinic acid in 165 ml 2.5% alcoholic solution of hydrogen chloride was hydrogenated at room temperature in presence of 0.63 g platinum oxide under a pressure of 40-60 cm water column. Absorption ceased after 9-10 hours. During hydrogenation the trihydrochloride of the di-(diethylaminoethyl) ester of dipipecolinic acid was precipitated. The precipitate was dissolved by addition of water, the catalyst was filtered off and washed with a little distilled water; the filtrate was evaporated to dryness in vacuum. The crystalline residue was treated with excess of 50% potassium carbonate solution and extracted with ether. After drying and removal of the ether, the residue was distilled in vacuum to give 9.3 g (86%) colorless, oily liquid with b.p. 182-184° (0.2 mm).

Found %: C 61.63; H 9.91; N 11.13. $C_{19}H_{37}O_4N_3$. Calculated %: C 61.45; H 9.97; N 11.32.

The trihydrochloride: a white, crystalline powder, m.p. 232-233°, soluble in water and alcohol.

Found %: C 47.16; H 8.58; N 8.54; Cl 21.99. $C_{19}H_{40}O_4N_3Cl_3$. Calculated %: C 47.45; H 8.32; N 8.74; Cl 22.16.

Diethyl ester of dipicolinic acid. 6 g of dipicolinyl dichloride, prepared as described above, was heated with 60 ml anhydrous alcohol 5 hours at the boil. The ester was isolated in the usual manner. Obtained 6.78 g (84.7%) crystalline substance, b.p. 127-128° (0.2 mm), m.p. 44-46°. The literature data give m.p. 41-42° [9].

Found %: C 59.61; H 6.07; N 6.40. $C_{11}H_{13}O_4N$. Calculated %: C 59.19; H 5.83; N 6.27.

Diethyl ester of dipipecolinic acid. A solution of 9.6 g diethyl ester of dipicolinic acid in 150 ml 2.5% alcoholic solution of hydrogen chloride was hydrogenated at room temperature in the presence of 0.4 g of platinum oxide under a pressure of 40-60 cm water column. After hydrogenation, the solution was worked up by the method described above. We isolated 8.86 g (90%) of colorless, oily product, b.p. 103-105° (0.25 mm).

Found %: C 57.38; H 8.43. $C_{11}H_{19}O_4N$. Calculated %: C 57.64; H 8.29.

Diethyl ester of N-methyldipipecolinic acid. A solution of 4.27 g of diethyl ester of dipipecolinic acid in 23 ml anhydrous alcohol and 1.32 g methyl iodide were heated 6 hours at 40-45°. The reaction mass was evaporated in vacuum on a boiling water bath and the residue extracted with anhydrous benzene. The benzene-insoluble crystals were the hydroiodide of the original ester. They were filtered off. Yield 2.85 g. The benzene was distilled off from the filtrate and the residue distilled in vacuum to give 2.39 g (52.7% reckoned on the ester) of colorless, oily substance with b.p. 107-108° (0.2 mm).

Found %: C 58.93; H 8.44; N 5.99. $C_{12}H_{21}O_4N$. Calculated %: C 59.26; H 8.64; N 5.76.

Di-(diethylaminoethyl) ester of N-methyldipipecolinic acid. 0.01 g metallic sodium was dissolved in 7 ml diethylaminoethanol and into this solution, with stirring, was run 1.32 g diethyl N-methyldipipecolinate. The reaction mass was heated with stirring for 3 hours at 150° and the ethyl alcohol which formed during this period was driven off with Wurtz head and direct condenser. The excess of diethylaminoethanol was distilled off in vacuum from the resulting solution, the residue was treated with an excess of 50% potash solution and extracted with ether. Yield 1.07 g (51.20%) yellow oily liquid with b.p. 176-178° (0.2 mm).

Found %: C 62.22; H 10.06; N 10.67. $C_{20}H_{39}O_4N_3$. Calculated %: C 62.33; H 10.13; N 10.90.

The methiodide and hydrochloride were oils.

Diethylaminoethyl ester of 6-methylpicolinic acid. This ester was obtained by a method similar to that for the di-(diethylaminoethyl) ester of dipicolinic acid in 77% yield. It is a light-yellow, oily substance with b.p. 128-131° (0.25 mm), soluble in the common organic solvents and insoluble in water.

Found %: N 11.94, 12.19. $C_{13}H_{20}O_2N_2$. Calculated %: N 11.86.

The hydrochloride is a white crystalline substance with m.p. 147-149°, hygroscopic.

The methiodide is a faint-yellow crystalline substance with m.p. 115-117° soluble in water, insoluble in ether and acetone.

Found %: N 7.26; I 33.74. $C_{14}H_{23}O_2N_2I$. Calculated %: N 7.40; I 33.58.

Diethylaminoethyl ester of 6-methylpipecolinic acid. 11.6 g diethylaminoethyl ester of 6-methylpicolinic acid was hydrogenated in 165 ml 2.5% alcoholic solution of hydrogen chloride in presence of 0.4 g platinum oxide under the conditions described above. There was obtained 6.17 g (52.3%) colorless, mobile liquid with b.p. 98-100° (0.2 mm).

Found %: C 64.20; H 10.86; N 11.40. $C_{13}H_{26}O_2N_2$. Calculated %: C 64.46; H 10.74; N 11.57.

The dihydrochloride is a white crystalline precipitate, soluble in water and alcohol and insoluble in ether, m.p. 220°.

Found %: Cl 22.39. $C_{13}H_{28}O_2N_2Cl_2$. Calculated %: Cl 22.53.

Ethyl ester of 6-methylpicolinic acid. The ester was prepared from 11.35 g of the acid chloride similarly to the diethyl ester of dipicolinic acid in amount of 10.48 g (87.3%). Colorless, oily substance with b.p. 79-81° (0.25 mm). The literature data give: b.p. 133° (35 mm) [10].

Found %: C 65.23; H 6.65; N 8.66. $C_9H_{11}O_2N$. Calculated %: C 65.45; H 6.66; N 8.48.

The hydrochloride is a white, hygroscopic, crystalline precipitate, soluble in water and alcohol, m.p. 74-75°.

Found %: Cl 17.81. $C_9H_{12}O_2NCl$. Calculated %: Cl 17.61.

Ethyl ester of 6-methylpipecolinic acid. 9.35 g ethyl 6-methylpicolinate was hydrogenated in 115 ml 2.5% alcoholic solution of hydrogen chloride in presence of 0.5 g platinum oxide under the conditions described above. There was obtained 8.84 g (92%) colorless, mobile liquid with b.p. 99-100° (13 mm).

Found %: N 8.56, 8.10. $C_9H_{17}O_2N$. Calculated %: N 8.18.

The hydrochloride is a white, finely crystalline substance with m.p. 213-215°, soluble in water and in hot alcohol, and insoluble in ether.

Found %: Cl 16.98. $C_9H_{18}O_2NCl$. Calculated %: Cl 17.10.

Ethyl 1,6-dimethylpipecolinate. A solution of 3.4 g ethyl 6-methylpipecolinate in 18 ml anhydrous alcohol and 1.37 g methyl iodide was heated 6 hours at 40-45° and then worked up as in the case of preparation of diethyl N-methylpipecolinate. There was obtained 1.5 g hydroiodide of the original ester and 1.65 g (43.7% reckoned on the ester) of a colorless, oily substance with b.p. 53-54° (0.2 mm).

Found %: C 64.76; H 10.31; N 7.85. $C_{10}H_{19}O_2N$. Calculated %: C 64.86; H 10.27; N 7.56.

The hydrochloride is an amorphous, hygroscopic solid with m.p. 198-200°.

Diethylaminoethyl ester of 1,6-dimethylpipecolinic acid. 0.02 g metallic sodium was dissolved in 20 ml diethylaminoethanol; addition was then made of 2.8 g ethyl 1,6-dimethylpipecolinate. The reaction mass was heated with stirring for $3\frac{1}{2}$ hours at 160-165° and then worked up as described for the preparation of the di-(diethylaminoethyl) ester of N-methylpipecolinic acid. There was obtained 1.65 g (44.7%) light-yellow, oily substance with b.p. 106-108° (0.25 mm).

Found %: N 10.83, 10.68. $C_{14}H_{28}O_2N_2$. Calculated %: N 10.93.

The dimethiodide is a white crystalline substance, soluble in water and alcohol, m.p. 201-202°.

Found %: N 5.32; I 47.07. $C_{16}H_{34}O_2N_2I_2$. Calculated %: N 5.18; I 47.03.

Diethylaminoethyl ester of α-quinuclidinecarboxylic acid. A mixture of 3 g α-quinuclidinecarboxylic acid hydrochloride [11] and 30 ml thionyl chloride was heated under reflux for 8 hours at 60-65°. The acid went into solution. The excess thionyl chloride was distilled off in vacuum and to the residue was added two lots of 15 ml anhydrous benzene which was then distilled off. The white crystalline precipitate of the hydrochloride of α-quinuclidinecarboxylic acid chloride was heated with stirring for 6 hours with 30 ml diethylaminoethanol at 110-115°. The excess of diethylaminoethanol was distilled off in vacuum, and the residue was treated with 15 ml 50% potassium carbonate solution and extracted with ether. After drying and removal of the ether, the residue was vacuum-distilled to give 2.85 g (73% reckoned on the hydrochloride of α-quinuclidinecarboxylic acid) of colorless oil with b.p. 160-164° (9 mm).

Found %: N 11.10, 11.08. $C_{14}H_{26}O_2N_2$. Calculated %: N 11.02.

The dimethiodide (from acetone) is a white crystalline substance with m.p. 222-223°, readily soluble in water, with more difficulty in alcohol, and insoluble in ether and acetone.

Found %: N 5.10; I 47.27. $C_{16}H_{32}O_2N_2I_2$. Calculated %: N 5.20; I 47.21.

SUMMARY

1. A series of alkamino esters of pyridine-, piperidine- and quinuclidinecarboxylic acids was synthesized.

2. Pharmacological study of the synthesized esters revealed that two members – the diethylaminoethyl esters of α-quinuclidinedicarboxylic acid and of 1,6-dimethylpipecolinic acid – in the form of their quaternary salts possess high ganglion-blocking activity.

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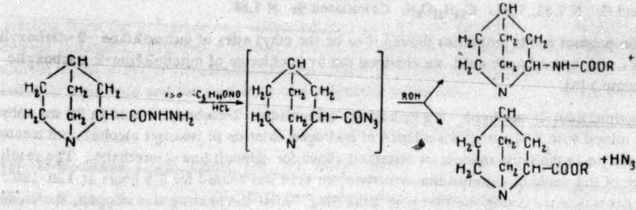
THE PREPARATION AND PROPERTIES OF ETHYL-N-(2-QUINUCLIDINYL)URETHANE

M. V. Rubstov and E. E. Mikhlina

As is known, α-aminopiperidine is stable in the form of its acyl derivatives [1, 2], but when attempts are made to isolate it in the free state the compound cleaves ammonia and is converted into a tetrahydropyridine polymer. As is shown in the present communication, a similar situation also exists for 2-aminoquinuclidine.

We made an attempt to obtain 2-aminoquinuclidine by the Curtius reaction. Our starting product was the hydrazide of 2-quinuclidinecarboxylic acid, which when reacted with isoamyl nitrite in alcoholic hydrogen chloride solution was converted into ethyl-N-(2-quinuclidinyl)urethane in 44% yield. Here the ethyl ester of 2-quinuclidinecarboxylic acid is formed as a by-product in about 25% yield. The reaction course can be depicted by the following scheme:



$R = C_2H_5$, iso-C_5H_{11}.

The hydrolysis of ethyl-N-(2-quinuclidinyl)urethane with hydrochloric acid gives the equivalent amount of ammonium chloride and an amorphous substance is formed, soluble in alcohol and in chloroform, and insoluble in other organic solvents and in water. This compound has the composition $C_7H_{11}N$, shows negative reaction for the double bond and, apparently, is a dehydroquinuclidine polymer.

Ammonia is evolved when ethyl-N-(2-quinuclidinyl)urethane is reacted at 180° with either aniline or benzylamine, and diphenyl- or dibenzylurea is formed; here the quinuclidine portion of the molecule is converted into a hard polymer, in its properties identical with the polymer that is formed when the urethane is treated with hydrochloric acid. If the reaction is run at 100° the products obtained are ammonia, the polymeric compound and benzylurethane. The latter when heated with benzylamine at 180° gives dibenzylurea. The formation of dibenzylurea when the urethane is heated with benzylamine at 180° is the result of a secondary reaction between the benzylurethane, already formed at 100°, and benzylamine. Apparently, the primary reaction is the transacylation that takes place between the ethyl-N-(2-quinuclidinyl)urethane and the benzylamine, as a result of which 2-aminoquinuclidine is formed. The latter compound, being an unsymmetrically substituted diaminomethane, cleaves one mole of ammonia to form an unsaturated bicyclic system, which suffers easy condensation and conversion into a hard polymer.

EXPERIMENTAL

Ethyl-N-(quinuclidyl-2)-urethane. 7.27 ml 16.4% alcoholic solution of hydrogen chloride was added to a solution of 3.76 g hydrazide of quinuclidine-2-carboxylic acid (m.p. 78°) in 40 ml anhydrous ethyl alcohol and then 3.88 g freshly prepared isoamylnitrite was added to the reaction mixture with ice cooling and stirring. After all the isoamyl nitrite was added, which took 20 minutes, the ice bath was removed and the reaction mixture was stirred at room temperature for 3 hours and the solution was then heated at the boil for 4 hours. The evolution of nitrogen stopped after 2 hours. The alcohol was steamed off in vacuum and the residue was treated with 50% potash solution and extracted with ether. The ethereal solution was dried with calcined potash for one hour and then the ether was driven off and the residue was heated over a boiling water bath for 30 minutes. The gelatinous mass which formed was carefully rubbed off and washed with dry ether. We isolated 1.9 g (44.3%) ethyl-N-(quinuclidyl-2)urethane in the form of white amorphous powder, difficulty soluble in alcohol and insoluble in water and other organic solvents. It melted at 166-168°.

Found %: C 60.56, 60.26; H 9.23, 9.02; N 14.34, 14.41. $C_{10}H_{18}O_2N_2$.
Calculated %: C 60.60; H 9.09; N 14.14.

The hydrochloride was obtained upon dilution of the product in 5% hydrochloric acid solution with acetone. M.p. 136-138° (from aqueous acetone). The white powder, readily soluble in water, was insoluble in acetone, ether and benzene.

Found %: N 11.60; Cl 15.16. $C_{10}H_{18}O_2N_2 \cdot HCl$. Calculated %: N 11.94; Cl 15.14.

The ethereal mother liquor, after separation of ethyl-N-(quinuclidyl-2)urethane, was steamed down in vacuum and the residue was distilled. We obtained 1 g colorless mobile liquid, readily soluble in water and in organic solvents. B.p. 87-89° (0.5 mm), 122-123° (14 mm), n_D^{23} 1.4723.

Found %: N 7.83, 7.91. $C_{10}H_{17}O_2N$. Calculated %: N 7.65.

Analysis of the product and it properties showed it to be the ethyl ester of quinuclidine -2-carboxylic acid. Upon hydrolysis with hydrochloric acid, we obtained the hydrochloride of quinuclidine-2-carboxylic acid, m.p. 300° (decomp.) [3].

Isoamyl-N-(quinuclidyl-2)-urethane. 2 g hydrazide quinuclidine-2-carboxylic acid in 20 ml anhydrous isoamyl alcohol was mixed with 2.75 ml 23.4% solution of hydrogen chloride in isoamyl alcohol and treated with 2.07 g isoamyl nitrite in the same manner as described above for quinuclidine-2-urethane. The resulting alcoholic solution of the azide of quinuclidine-2-carboxylic acid was heated for 3.5 hours at 120-125°. Intense evolution of gas was noted during the first hour of heating. After the heating was stopped, the isoamyl alcohol was driven off under reduced pressure, the residue was dissolved in 5 ml water, the aqueous solution was treated with 20 ml 50% potash solution and extracted with ether. The ethereal solution was dried over sodium sulfate, the ether was driven off and the substance was distilled in vacuum. The liquid collected at 0.6 mm boiled at 100-137° and was separated into two fractions by a second distillation which boiled at 105-108° and 110-112°. The 1st fraction (0.95 g), a greenish liquid, readily soluble in organic solvents, less soluble in water, was isoamyl-N-(quinuclidyl-2-)-urethane; n_D^{16} 1.4587.

Found %: C 64.84, 64.90; H 10.21, 10.19. $C_{13}H_{24}O_2N_2$. Calculated %: C 65.00; H 10.00.

The 2nd fraction (0.8 g), a colorless liquid, readily soluble in organic solvents and in water, was the isoamyl ester of quinuclidine-2-carboxylic acid; n_D^{16} 1.4671.

Found %: C 69.03; H 10.58. $C_{13}H_{23}O_2N$. Calculated %: C 69.33; H 10.22.

Hydrolysis of ethyl-N-(quinuclidyl-2)-urethane with hydrochloric acid. 1 g ethyl-N-(quinuclidyl-2)-urethane and 10 ml of hydrochloric acid (1 : 1) were heated at the boil for 4 hours. The cooled solution was filtered, concentrated in vacuum, the residue was diluted with acetone and 0.26 g of ammonium chloride was filtered off. The mother liquor was steamed down after separation of the crystals; the residue was treated with 50% potash solution and extracted with chloroform. The amorphous precipitate, obtained upon removal of the chloroform, was dissolved in 5 ml of alcohol and mixed with 10 ml alcoholic solution of picric acid. The picrate which came down was separated, washed with alcohol and dried. It was a yellow powder, m.p. 158-160°.

Found %: C 45.99, 46.06; H 4.30, 4.60 $(C_7H_{11}N \cdot C_6H_3O_7N_3)_n$. Calculated %: C 45.90; H 4.16.

Reaction of ethyl-N-(quinuclidyl-2)-urethane with benzylamine. a) 1 g ethyl-N-(quinuclidyl-2)-urethane and 6 g benzylamine were heated at 180° for 6 hours. The reaction solution had an ammonia odor. Upon cooling, long colorless needles fell down, were spearated off, washed with a small quantity of alcohol and recrystallized two times from alcohol. They melted at 167-168° [4]. Yield 0.9 g. The substance was not soluble in water or in hydrochloric acid. Analysis of the compound and its properties showed it to be dibenzylurea.

Found %: C 74.85, 75.13; H 6.83, 6.72; N 11.50. $C_{15}H_{16}ON_2$. Calculated %: C 75.00; H 6.67; N 11.67.

After separating the dibenzylurea, the mother liquor was concentrated under reduced pressure. After the benzylamine was driven off, the residue was a foamy mass, soluble in alcohol and insoluble in other organic solvents and water. The prepared picrate melted at 158-160° (decomp.) and was identical to the picrate prepared from the polymer which formed upon treating ethyl-N-(quinuclidyl-2)-urethane with hydrochloric acid.

b) A mixture of 1 g ethyl-N-(quinuclidyl-2)-urethane and 6 g benzylamine was heated on a boiling water bath for 10 hours. The ammonia which evolved was detected by odor and blueing of litmus. The reaction mixture was concentrated under reduced pressure. Benzylamine at first, and then benzylurethane were driven off. B.p. 50-52° (0.3 mm) and m.p. 45°. The above-described polymer remained in the distilling flask.

Found %: N 7.76. $C_{10}H_{13}O_2N$. Calculated %: N 7.82.

The distilled benzylurethane (0.4 g) was heated with 3 g of benzylamine at 180° for 6 hours. Dibenzylurea came down. M.p. 167-168°.

SUMMARY

Starting from the hydrazide of 2-quinuclidinecarboxylic acid the ethyl- and isoamyl-N-(2-quinuclidinyl)-urethanes were obtained. Together with the urethanes the esters of 2-quinuclidinecarboxylic acid are formed. The treatment of the ethyl-N-(2-quinuclidinyl)-urethane with either hydrochloric acid or benzylamine leads to the evolution of ammonia and the formation of a polymeric substance.

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Found %. C [illegible]

Calcd. for [illegible]

[illegible] at 100° for 4 hours. [illegible] recrystallized from alcohol. [illegible] soluble in water [illegible]

[illegible]

After [illegible] the polymer [illegible]

[illegible]

[illegible]

Summary

[illegible]

(1) [illegible]

(2) [illegible]

(3) [illegible]

(4) [illegible]

[illegible]

[illegible] polymer [illegible]

[illegible]

THE STABILITY OF THE Si-C BOND IN AROMATIC AND HYDROAROMATIC SILANES TO THE ACTION OF ACIDIC REAGENTS

A. D. Petrov, T. I. Chernysheva and E. A. Chernyshev

The Si-C_{aryl} bond differs sharply from the C−C bond in its behavior toward heterolytic (ionic) decomposition, proceeding easily under the influence of either acids or alkalies, which is determined by the larger volume and lower electronegativity of the Si atom when compared with the carbon atom (the electronegativity of silicon is 1.8, that of carbon is 2.5) [1]. The stability of this bond also changes within certain limits as a function of the electronegativity (magnitude) of the radical in which the carbon atom is found. The radicals, situated to the right of phenyl in the radical series, arranged in the order of decreasing negative charge [2], show relatively stable bonding to silicon, and in these cases the Si-C bond is not destroyed by acidic reagents. In addition, concentrated sulfuric acid is frequently used to purify tetraalkylsilanes. Excluded from the radicals standing to the right of phenyl are the allyl, the alkynyls and phenylethynyl, all suffering cleavage under the influence of acids [3]. However, it is possible that the decomposition of such compounds is due to the instability (at room temperatures) of the addition products of the acidic reagents at the multiple bonds as the result of β-decomposition.

The aromatic radicals − phenyl and the radicals standing to the left of it, and characterized by negative charges of considerable magnitude, present a different story. Even phenyl itself is cleaved with extreme ease under the influence of dry HCl in acetic acid under the standard conditions used for studying the stability of the Si-C bond [4]. An even stronger reagent − aluminum chloride − quantitatively cleaves the Si-C_{phenyl} bond even at room temperature [5].

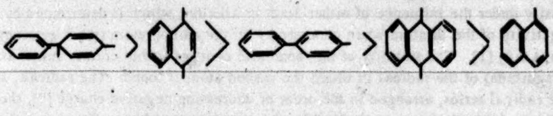
For the aromatic silanes with substituents in the ring the stability of the Si-C bond toward the action of acidic reagents is first determined by the nature of the substituent. It was found that the higher the Hammet constant σ of the substituent, characterizing the charge of the latter [6], the greater the stability of the Si-C bond; in this connection the presence of a substituent with $\sigma > +0.4$ strengthens the Si-C_{aryl} bond to such an extent that it fails to suffer rupture under the influence of electrophilic reagents [7]. Substituents with such a value are very few − the main ones are m-CN (+ 0.678), p-CN (+1.000), m-NO_2 (+0.710), p-NO_2 (+0.778), p-COOH (+0.728), p-CH_3CO (+0.874), p-CHO (+1.126). Because of the stability of compounds with such substituents it proved possible, for example, to acylate toluene and anisole with the acid chlorides of o- and p-trimethylsilylbenzoic acids in the presence of $AlCl_3$ [8].

The aralyky radicals, in which the aryl group is linked with Si through an aliphatic bridge, such as benzyl, β-phenylethyl, etc., are located right of aliphatic radicals in the radical electronegative series. And actually, the Si-C bond in the silanes with such radicals proved to be extremely resistant to the action of acidic reagents. Hydrogen chloride under the above presented standard conditions is completely without effect on either trimethylbenzylsilane or trimethyl-β-phenylethylsilane [4]. Aluminum chloride at temperatures up to 130-140° also fails to evoke decomposition of the Si−C bond in either the benzyl- or β-phenylethylsilanes, which fact made it possible for us to synthesize the latter by the silicoalkylation of aromatic hydrocarbons with α- and β-chloroalkyltrichlorosilanes [9], and also to acylate trimethylbenzylsilane [10] in the presence of $AlCl_3$.

In the present work we were interested in studying the behavior of the hydroaromatic silanes, i.e. the "intermediates" between the aromatic and aliphatic silanes, toward HCl and $AlCl_3$. We studied the reaction of 1,4-di-(tributylsilyl)-1,4-dihydrobiphenyl, 1,4-di-(triethylsilyl)-1,4-dihydronaphthalene and 9,10-di-(triethylsilyl)-9,10-dihydroanthracene with 20% HCl, dry hydrogen chloride in glacial acetic acid, and ammonium chloride. For comparison we also studied the behavior in these reactions of the structurally similar aromatic silanes − triethylbiphenylsilane and triethylnaphthylsilane.

When triethylnaphthylsilane was boiled with an excess of 20% HCl the $Si-C_{naphthyl}$ bond was destroyed to the extent of 89%. The other 4 investigated compounds proved to be stable under these conditions and absolutely no destruction of the Si−C bond was observed.

The reaction with dry hydrogen chloride was run under the standard conditions used to study the stability of the Si−C bond. The silicohydrocarbon was dissolved in an an approximately equal amount of acetic acid, and dry hydrogen chloride was passed through the mixture for 6 hours. Under these conditions the triethylnaphthyl- and triethylbiphenylsilanes suffered decomposition to the extent of 84 and 43%, respectively. The 9,10-di-(triethylsilyl)-9,10-dihydroanthracene showed decomposition to the extent of 72%, in which connection the crystalline decomposition product consisted of 80% anthracene and 20% dihydroanthracene, i.e. dehydrogenation proceeded parallel with the cleavage reaction. Under these conditions the 1,4-di-(triethylsilyl)-1,4-dihydronaphthalene showed a total decomposition of only 10%, in which connection the crystalline decomposition product was pure naphthalene. 1,4-Di-(tributylsilyl)-1,4-dihydrobiphenyl was completely unaffected under these conditions. As a result, in the stability of the Si−C bond toward the action of HCl, the radicals of the investigated compounds can be arranged in the following order:



To study the reaction of the silanes with aluminum chloride the silicohydrocarbon and an equivalent amount of $AlCl_3$, needed for complete cleavage of the $Si-C_{hydroaryl\ (aryl)}$ bond, were placed in a flask, and the mixture was stirred at 15-25° for 15 hours. In all cases quantitative cleavage of the $Si-C_{hydroaryl\ (aryl)}$ bond was observed. It should be mentioned that in the case of the dihydroaromatic silanes only aromatic hydrocarbons were present in the decomposition products, i.e. parallel with the cleavage of the Si−C bond there proceeded quantitative dehydrogenation.

EXPERIMENTAL

Silicon hydrocarbons were synthesized by the previously described methods [11, 12].

1) Reaction of silicon hydrocarbons with 20% HCl. 5.5 g triethylnaphthylsilane and 10 ml 20% HCl was placed in a round-bottomed flask fitted with reflux condenser. The contents of the flask were boiled for 3 hours. The mixture was then cooled and the naphthalene was filtered off, washed on a filter with water, with weak $NaHCO_3$ solution and recrystallized from alcohol. We isolated 2.55 g (89%) naphthalene. It melted at 79.5-80°. A test mixture gave no depression.

Silicon Hydrocarbon	Taken for reaction (g)	Isolated in reaction (g)	Boiling point		n_D^{20}	
			of initial compounds	of isolated compounds	of initial compounds	of isolated compounds
Triethylxenylsilane	10	7.0	145-147° (3 mm)	140-145° (3 mm)	1.5668	1.5670
1,4-Di-(tributylsilyl)-1,4-dihydrobiphenyl	15	12.2	223-225 (20 mm)	218-222 (19 mm)	1.4770	1.4768
1,4-Di-(triethylsilyl)-1,4-dihydronaphthalene	15	11.7	320-322	318-322	1.5238	1.5230
9,10-Di-(triethylsilyl)-9,10-dihydroanthracene *	10	7.3	234 (3 mm)	234-237 (3 mm)	–	–

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* Original substance had m.p. 79.5°, isolated − 78-79°.

The Si—C bond remained intact in the other four cases. The experiments were performed under the same conditions. After cooling the mixture, the organic layer was separated off and the acid layer was extraced with ether. The organic layer and the ethereal extract were washed with water and weak $NaHCO_3$ solution, dried and distilled. The experimental results are given in the table.

2) Reaction of silicon hydrocarbons with dry HCl in acetic acid. a) Triethylnaphthylsilane. 5 g of silicon hydrocarbon was dissolved in 10 ml of glacial acetic acid. A stream of dry HCl was passed into the solution for 6 hours. The mixture was then poured into weak $NaHCO_3$ solution. The naphthalene which came down was filtered off, washed over filter paper with water and weak $NaHCO_3$ solution and recrystallized from alcohol. We isolated 2.2 g naphthalene, m.p. 79.5°. A test mixture gave no depression.

b) Triethylxenylsilane. 7 g silicon hydrocarbon was dissolved in 12 ml glacial acetic acid. The reaction was performed under the same conditions as in Experiment (a). Yield 1.7 g (43%) diphenyl, m.p. 68.5°. A test mixture gave no depression.

c) 1,4-Di-(tributylsilyl)-1,4-dihydrobiphenyl. 6.5 g silicon hydrocarbon was dissolved in 12 ml of glacial acetic acid. The reaction was performed under the conditions of Experiment (a). When the reaction mixture was poured into water, a crystalline product did not form. The organic layer was separated, washed with water and with $NaHCO_3$ solution and dried. Distillation yielded 4.7 g 1,4-di-(tributylsilyl)-1,4-dihydrobiphenyl which boiled at 218-225° (20 mm), n_D^{20} 1.4765.

d) 1,4-Di-(triethylsilyl)-1,4-dihydronaphthalene. 12 g silicon hydrocarbon was dissolved in 20 ml glacial acetic acid and a stream of dry HCl was passed through the solution for 10 hours. When the mixture was poured in water, some crystalline product formed and a large organic layer remained. After suitable treatment of the crystalline product, we isolated 0.20 g crystals, m.p. 78.5-79°. Distillation of the organic layer yielded 0.23 g more crystals, m.p. 77-79° and 7.6 g initial silicon hydrocarbon, boiling range 315-325°, n_D^{20} 1.5235. After recrystallization from alcohol the crystals melted at 79.5°. A test mixture with naphthalene gave no depression.

e) 9,10-Di(triethylsilyl)-9,10-dihydroanthracene. 7.5 g silicon hydrocarbon was dissolved in 15 ml glacial acetic acid. A stream of dry HCl was passed through the solution for 6 hours. The contents of the flask were then poured into water and neutralized with soda. The reaction products were extracted with ether, dried and distilled. Distillation yielded 0.45 g 9,10-dihydroanthracene, b.p. 310-315°, m.p. 106° (from alcohol). A test mixture gave no depression. We also isolated 1.9 g anthracene, boiling range 342-355°, m.p. 215-218° (a test mixture gave no depression), and 3.8 g initial silicon hydrocarbon, b.p. 230-234° (3 mm), m.p. 78.5°. Thus, the decomposition amounted to 72% (based on the decomposition products).

3) Reaction of silicon hydrocarbons with aluminum chloride. a) Triethylnaphthylsilane. We placed 10 g silicon hydrocarbon and 5.5 g $AlCl_3$ in a small flask fitted with a stirrer. The mixture was stirred for 10 hours at 20-25° and decomposed upon careful pouring over finely ground ice. The organic layer was extracted with benzene, dried and distilled. Distillation yielded 4.9 g (~93%) naphthalene, m.p. 79.5°. A test mixture gave no depression. Besides this, we isolated 1.6 g triethylsilanol, b.p. 153-158°, n_D^{20} 1.4360 and 2 g hexaethyldisiloxane, b.p. 230-235°, n_D^{20} 1.4345.

b) Triethylxenylsilane. 10 g silicon hydrocarbon and 5 g $AlCl_3$ were placed in a small flask fitted with a stirrer. The reaction was performed under the conditions of Experiment (3a). Distillation yielded 5.1 g (90%) biphenyl, m.p. 68-69°. A test mixture gave no depression. Besides this, we isolated 2.8 g hexaethyldisiloxane, b.p. 220-228°, n_D^{20} 1.4342.

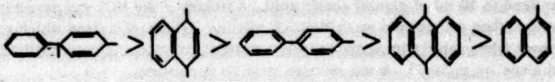
c) 1,4-Di-(tributylsilyl)-1,4-dihydrobiphenyl. We took 12 g silicon hydrocarbon and 5.8 g $AlCl_3$ for the reaction. The reaction was performed under the conditions of Experiment (3a). Distillation yielded 2.6 g biphenyl, m.p. 68.5 (a test mixture gave no depression) and 5.3 g hexabutyldisiloxane, b.p. 193-194° (10 mm), n_D^{20} 1.4438.

d) 1,4-Di-(triethylsilyl)-1,4-dihydronaphthalene. We took 10 g silicon hydrocarbon and 7.4 g $AlCl_3$ for the reaction. The reaction was performed under the conditions of Experiment (3a). Distillation yielded 3.05 g (85%) naphthalene, m.p. 80° (a test mixture gave no depression), and also 2.1 g of triethylsilanol, b.p. 152-156°, n_D^{20} 1.4365 and 2 g hexaethyldisiloxane, boiling range 230-235°, n_D^{20} 1.4346.

e) 9,10-Di(triethylsilyl)-9,10-dihydroanthracene. 8.2 g silicon hydrocarbon and 5.3 g of $AlCl_3$ were taken for the reaction. Distillation yielded 3.1 g (86%) of anthracene, m.p. 214° (a test mixture gave no depression) and 3.8 g hexaethyldisiloxane, b.p. 230-238°, n_D^{20} 1.4349.

SUMMARY

1. With respect to the action of HCl in glacial acetic acid the hydroaromatic silanes are more stable than are their structurally similar aromatic silane analogs. In the stability of the Si—C bond to the action of HCl the investigated radicals can be arranged in the following order:



2. Aluminum chloride effects quantitative cleavage of both the aromatic and hydroaromatic silanes studied by us.

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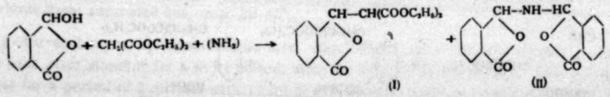
THE CONDENSATION OF o-ALDEHYDOBENZOIC ACID AND ITS METHYL ESTER WITH MALONIC ESTER

V. M. Rodionov* and E. I. Chukhina

In 1926 V. M. Rodionov and his coworkers found a simple and original method for the preparation of β-aryl-β-aminopropionic acids, consisting in the condensation of aromatic aldehydes with malonic acid in the presence of alcoholic ammonia solution [1]. Under these conditions the unsaturated acid is formed in equal amount, and at times predominantly. This synthesis was successfully extended to the aliphatic aldehydes [2] and the aromatic aldehydo acids [3]. The condensation of the aldehydo acids was studied with both the neutral and partial malonic esters [4].

As was shown by V. M. Rodionov and A. M. Fedorova [3], the main reaction product in the condensation of dimethoxy-o-aldehydobenzoic acid (opianic acid) with malonic ester in the presence of alcoholic ammonia solution is meconylmalonic ester, and the amino acid derivative is not formed at all.

In the present work we studied the condensation of malonic ester with o-aldehydobenzoic acid – the analog of opianic acid, having become more readily available in recent years [5]. When this reaction was run under the same conditions as for opianic acid, the corresponding phthalidylmalonic ester (I) was also isolated and as a secondary product of the reaction there was obtained a nitrogen-containing compound, in accord with its analysis data being diphthalidylamine (II). The desamination of this compound (the amine) by treatment with HNO_2 gave o-aldehydobenzoic acid in quantitative yield:



The reaction of o-aldehydobenzoic acid with malonic ester was also studied under other conditions. When the ammonia was replaced by piperidine only the ethyl ψ-ester of o-aldehydobenzoic acid was isolated. When the condensation of malonic ester with o-aldehydobenzoic acid was run in the presence of pyridine [6], instead of the phthalidylmalonic ester the isomeric o-carboxybenzylidenemalonic ester (III) was obtained, being soluble in soda and decolorizing bromine water. The heating of this ester with alcoholic caustic solution gave o-carboxycinnamic acid; the same acid was also isolated when the ester was heated with alcoholic sodium ethylate solution.

From the literature it is known that o-aldehydobenzoic acid reacts in two tautomeric forms – as an aldehydo acid and as a hydroxy lactone [7]. In order to develop the question as to which tautomeric forms are capable of yielding the isomeric esters obtained by us, we undertook a study of the isomerization of these compounds. The studies revealed that when the phthalidylmalonic ester (I) is heated with pyridine, i.e. under the conditions for the preparation of its isomeric compound (III), that this ester remains unchanged. If the o-carboxybenzylidenemalonic ester (III) is heated in alcoholic ammonia solution, then it is isomerized, forming the phthalidylmalonic ester (I). Finally, it was established that when the o-carboxybenzylidenemalonic ester (III) is heated to 200-210° without solvent that it fails to suffer any changes whatsoever; in this respect it is quite different from the o-carboxycinnamic acid, which easily isomerizes to phthalidylacetic acid when heated to 197° [8]. These results permit the conclusion that the o-carboxybenzylidenemalonic ester (III) can be formed only from the aldehydo acid form to o-aldehydobenzoic acid. As regards the formation of the phthalidylmalonic ester (I), then it can be formed by either the direct condensation of the hydroxy lactone form of o-aldehydobenzoic acid or by the secondary isomerization of the first formed o-carboxybenzylidenemalonic ester (III):

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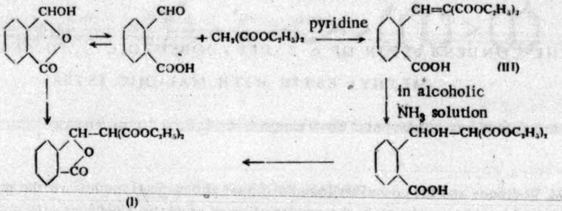
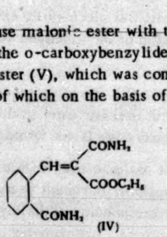
* Deceased

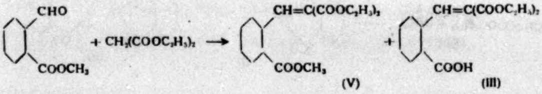


Attempts were made to condense malonic ester with the methyl α-ester of o-aldehydobenzoic acid. Here, Here, as in the preceding instance, the o-carboxybenzylidenemalonic ester (III) was isolated, and in small amount apparently also the methyl ester (V), which was converted by treatment with aqueous ammonia solution into the diamide, the structure of which on the basis of its analysis data corresponds to Formula (IV):



(IV)

The presence of a comparatively large amount of the o-carboxybenzylidenemalonic ester in the reaction products is probably associated with the facile hydrolysis of its carbomethoxyl group.



EXPERIMENTAL

Condensation of o-aldehydobenzoic acid with malonic ester. a) In alcoholic ammonia solution. A mixture of 11 g o-aldehydobenzoic acid, 11.73 g malonic ester and 20 ml alcoholic 12% solution of ammonia was heated over a water bath for 5 hours. After the condensation product was treated with absolute ether, we isolated 1.85 g diphthalidylamine, insoluble inether. It was in the form of colorless needles (from alcohol), soluble in alkali and in concentrated HCl. M.p. 200-201°.

Found %: C 68.52, 68.44; H 3.92, 3.86; N 5.12, 5.06. $C_{12}H_{11}O_4N$. Calculated %: C 68.32; H 3.91; N 4.98.

0.06 g $NaNO_2$ was added in small portions with ice-water cooling to 0.18 g diphthalidylamine which had been acidified with 6 drops 10% H_2SO_4 solution. The mixture was then heated until the solid substance dissolved. After the acidic solution was evaporated down, 0.18 g o-aldehydobenzoic acid separated out.

Upon treatment of the ethereal solutions with alcoholic ammonia solution, after the ether and alcohol were driven off, 15.45 g of oil separated out which crystallized upon standing. The obtained phthalidylmalonic ester crystallized from aqueous alcohol in the form of fine colorless needles which melted at 89-90°; the substance did not dissolve in soda but dissolved in alkali.

Found %: C 61.51, 61.71; H 5.42, 5.53. $C_{15}H_6O_6$. Calculated %: C 61.64; H 5.48.

b) In alcoholic solution in the presence of piperidine. Addition of 6 drops of piperidine to a mixture of 5 g o-aldehydobenzoic acid and 5.33 g malonic ester in 30 ml of absolute alcohol with heating for 5.5 hours yielded 3.2 g ψ-ester of o-aldehydobenzoic acid.

c) In the presence of pyridine. 25. g o-aldehydobenzoic acid, 26.7 g malonic ester and 3 g pyridine were heated for a period of 10 hours on an oil bath at 107-115°. The resulting oil was first mixed with 80 ml water and then with 19 ml 18% HCl solution and shaken with ether. From the ethereal layer, washed with 10-12% soda solution and with water, after the ether was driven off, 40.1 g viscous oil separated out which after fractional crystallization, yielded 30.1 g o-carboxybenzylidenemalonic ester, m.p. 39-40°. *

Found %: C 61.64, 61.59; H 5.48, 5.58. M 300. ** $C_{15}H_6O_6$. Calculated %: C 61.64; H 5.48. M 292.

0.5 g o-carboxybenzylidenemalonic ester was heated with 15 ml 5% alcoholic KOH solution for 3 hours; after the oil which formed dissolved in water and the resulting solution was acidified, 0.3 g o-carboxycinnamic acid separated out. The same o-carboxycinnamic acid (0.2 g) was prepared from o-carboxybenzylidenemalonic ester (0.35 g) upon heating the latter with 6 ml sodium ethylate (0.18 g) in alcoholic solution.

By heating 2.0 g o-carboxybenzylidenemalonic ester in alcoholic ammonia solution under the conditions of synthesis of its isomer (see Experiment a), we obtained 1.35 g phthalidylmalonic ester, 0.18 g o-aldehydobenzoic acid and 0.31 g initial ester. This ester remained unchanged upon being heated to 210°.

0.8 g initial ester was obtained by heating 1.0 g phthalidylmalonic ester with pyridine for 10 hours.

Condensation of methyl o-aldehydobenzoate *** with malonic ester. 10.28 g of oil was obtained under the same conditions used to synthesize o-carboxybenzylidenemalonic ester from 5.45 g of methyl o-aldehydobenzoate, 5.32 g malonic ester and 0.5 g pyridine. When this oil was distilled, 0.6 g of the methyl ether of o-carboxybenzylidenemalonic ester, b.p. 235-237° at 8 mm, separated out.

The residue (2.5 g), boiling higher than 237° at 8 mm, crystallized upon standing. o-Carboxybenzylidenemalonic ester separated out, m.p. 39-40°.

0.13 g of o-carboxybenzylidenemalonic ester, m.p. 39-40°, obtained from 0.2 g of its methyl ether, dissolved in soda after standing for a short period, after the solution was acidified. After setting aside 0.2 g of the ether for a period of 2 months with 10 ml of 37% aqueous ammonia and evaporating down the solution almost to dryness, 0.1 g of diamide (IV) separated out. It crystallized from the aqueous alcohol in the form of transparent flakes of irregular form which turned brown upon charring but did not fuse when heated to 300°.

Found %: C 60.00, 60.10; H 5.10, 5.05; N 10.60, 10.67. $C_{13}H_{14}O_4N_2$. Calculated %: C 59.54; H 5.34; N 10.68.

SUMMARY

1. Depending on the conditions used for the condensation of o-aldehydobenzoic acid with malonic ester it was found that two isomeric compounds are formed – the phthalidylmalonic ester (in the presence of alcoholic ammonia solution) and the o-carboxybenzylidenemalonic ester (in the presence of pyridine).

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* 2.2 g o-aldehydobenzoic acid with a small admixture of o-carboxybenzylidenemalonic ester and 0.5 g o-carboxycinammic acid precipitated out of the soda solutions.

** The molecular weight was determined by cryoscopic method in benzene.

*** Methyl o-aldehydobenzoate was prepared from the silver salt of the acid upon heating it with CH_3I in dry benzene [9].

2. It was established that the phthalidylmalonic ester in the presence of pyridine cannot isomerize into the o-carboxybenzylidenemalonic ester, whereas the latter is isomerized in alcoholic ammonia solution, being converted into the more stable phthalidylmalonic ester.

3. On the basis of the performed studies it can be concluded that the o-carboxybenzylidenemalonic ester is formed only from the aldehydo acid form of o-aldehydobenzoic acid, while it is possible for the phthalidylmalonic ester to be formed from either hydroxyphthalidic acid or the aldehydo acid form of this acid.

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ABSORPTION SPECTRA AND STRUCTURE OF BENZENE DERIVATIVES

XVIII. 3,4-DIHYDROXYACETOPHENONE AND ITS METHYL ETHERS

N. A. Valyashko* and N. N. Valyashko

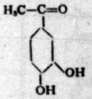
In the systematic study of the isomeric dihydroxyacetophenones for the purpose of eludicating the complex conjugation that exists between the benzene ring and the two hydroxyl groups and one carbonyl group the compounds that have already been studied are the 2,4- [1], 3,5- and 2,6-dihydroxyacetophenones [2]; still remaining unstudied are the 3,4-, 2,5- and 2,3-dihydroxyacetophenones.

In this paper we discuss the absorption spectra of 3,4-dihydroxyacetophenone and its methyl ethers.

The following compounds were synthesized by methods given in the literature: 3,4-dihydroxyacetophenone [3], 3-methoxy-4-hydroxyacetophenone [4], 3-hydroxy-4-methoxyacetophenone [5] and 3,4-dimethoxyacetophenone [6]. Prior to study the obtained substances were recrystallized from suitable solvents.

Spectrographic Studies

3,4-Dihydroxyacetophenone was studied spectrographically in ethanol, water and dichloroethane at concentrations of $2\cdot10^{-3}-2\cdot10^{-5}$ M. This compound is insoluble in hexane.

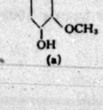


Due to the conjugation of the carbonyl group with the benzene ring and separately with the hydroxyl groups the absorption spectrum of 3,4-dihydroxyacetophenone in ethanol consists of the following bands: φ with a maximum at λ 2760 A and ϵ 10000, corresponding to the absorption band φ of 4-hydroxyacetophenone, α_2 (maximum at λ 3070 A and ϵ 8000) and α'_1 (maximum at λ 2300 A and ϵ 20000), corresponding to the absorption bands α_2 and α'_1 of 3-hydroxyacetophenone. The φ-band of 3,4-dihydroxyacetophenone is 2.5 times less intense than φ-band of 4-hydroxyacetophenone, while the α_2-band is twice as intense as the α_2-band of 3-hydroxyacetophenone (Fig. 1, Curves 1, 2 and 3).

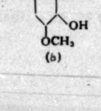
Solvents show quite a considerable effect on the absorption spectrum of 3,4-dihydroxyacetophenone. While retaining its general absorption character the absorption spectrum of 3,4-dihydroxyacetophenone, and especially the α_2-band, suffers in water, ethanol and dichloroethane solutions a successive shifting in the indicated order toward the short wavelengths and a considerable increase in band intensity in water when compared to the absorption bands in dichloroethane: α_2 being 1.25 and φ being 2.5 times greater (Fig. 2, Curves 1, 2 and 3).

A greater association of the 3,4-dihydroxyacetophenone molecule is possible in dichloroethane due to hydrogen bonding, while in water the intramolecular hydrogen bonds will be disturbed to a certain degree, and the conjugation of the hydroxyl with the benzene ring and the carbonyl group will increase, which leads to reinforcement of the φ-band.

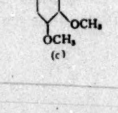
Methyl Ethers of 3,4-Dihydroxyacetophenone



(a)



(b)



(c)

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* Deceased.

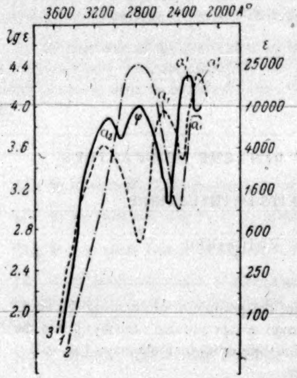


Fig. 1. 1) 3,4-dihydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 10^{-5}$M.,2) 4-hydroxyacetophenone in ethanol $10^{-2} - 2 \cdot 10^{-5}$M., 3) 3-hydroxyacetophenone in ethanol $10^{-2} - 2 \cdot 10^{-5}$ M.

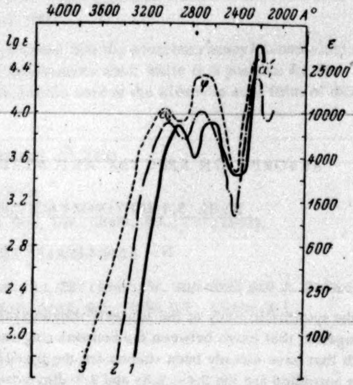


Fig. 2. 1) 3,4-dihydroxyacetophenone in dichloroethane $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M., 2) 3,4-dihydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M., 3) 3,4-dihydroxyacetophenone in water $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M.

TABLE 1

Compounds (Solutions in Ethanol)	a_2-band		φ-band		a'_1-band	
	λ	ε	λ	ε	λ	ε
3,4-Dihydroxyacetophenone	3070	8000	2760	10000	2300	20000
3-Methoxy-4-hydroxyacetophenone	3080	10000	2750	20000	2290	40000
3-Hydroxy-4-methoxyacetophenone	3100	11000	2740	16000	2310	40000
3,4-Dimethoxyacetophenone	3000	12000	2720	15000	2300	20000

3-Methoxy-4-hydroxy- (a), 3-hydroxy-4-methoxy- (b) and 3,4-dimethoxyacetophenone (c) were studied in water, ethanol and hexane at concentrations of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M. The conjugation character of 3,4-dihydroxyacetophenone is also retained in the molecules of its methyl ethers (Table 1).

It is interesting to mention that in the absorption spectrum of 3-methoxy-4-hydroxyacetophenone in ethanol the absorption band φ becomes twice as intense as the φ-band in the absorption spectrum of 3,4-dihydroxyacetophenone. This indicates that with methylation of the hydroxyl group in position 3 the hydroxyl in position 4 receives greater freedom for conjugation with the ring and carbonyl group. The interaction between the hydroxyl groups can be depicted in the form of an intramolecular hydrogen bond.

It is possible that this is also responsible for the increase in the intensity of the 3-methoxy-4-hydroxyacetophenone a_2-band by 1.25 in ethanol and by 1.5 in water when compared with the a_2-band of 3,4-dihydroxyacetophenone in the same solvents.

While retaining the general absorption character, the solvents cause slight changes in the positions of the absorption bands and in their intensities (Table 2).

3-Methoxy-4-hydroxy-, 3-hydroxy-4-methoxy- and 3,4-dimethoxyacetophenone in hexane solutions give spectra in which the a_2- and φ-bands are shifted toward the short wavelengths. The φ-band changes its intensity from ε 10000 to ε 16000, while the intensity of the a_2-band decreases from ε 10000 to ε 6000.

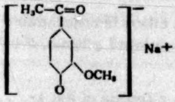
TABLE 2

Compound	Solvent	a_2-band		φ-band		a'_1-band	
		λ	ε	λ	ε	λ	ε
3-Methoxy-4-hydroxyacetophenone	Water	3020	15000	2740	22000	2270	45000
3-Methoxy-4-hydroxyacetophenone	Hexane	2890	10000	2640	10000	2225	45000
3-Hydroxy-4-methoxyacetophenone	Water	3090	11000	2750	16000	2320	20000
3-Hydroxy-4-methoxyacetophenone	Hexane	2980	6000	2620	12500	2260	32000
3,4-Dimethoxyacetophenone	Water	3000	11000	2750	16000	2300	20000
3,4-Dimethoxyacetophenone	Hexane	2980	6400	2690	16000	2800	20000

3,4-Dihydroxyacetophenone and its methyl ethers in alkaline solutions. Under the influence of sodium ethanolate in ethanol the monomethyl ethers of 3,4-dihydroxyacetophenone give salt-like compounds at the unmethylated hydroxyl group, in which connection the corresponding band, the same as in the formation of the salts of the monohydroxyacetophenones, is shifted considerably toward the long wavelengths, which indicates that both of the conjugations in the 3,4-dihydroxyacetophenone molecule retain the properties of the monohydroxyacetophenones to a certain degree.

For 3-methoxy-4-hydroxyacetophenone in ethanol in the presence of 100 mole equivalents of sodium ethanolate a salt is formed at the hydroxyl group in position 4, in which connection there occurs full development of the absorption band φ with its shifting by 370 A toward the long wavelengths (Fig. 3, Curve 1). Under influence of 10 mole equivalents of sodium ethanolate the 3-methoxy-4-hydroxyacetophenone in ethanol solution gives the same position for the absorption band φ, but it is one-half as intense as in the case of 100 mole equivalents of sodium ethanolate (Fig. 3, Curve 2). In addition, on this absorption spectrum curve there appears a flat bend, corresponding to the absorption region of 3-methoxy-4-hydroxyacetophenone in neutral ethanol.

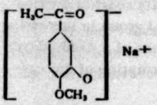
That incomplete salt-formation is obtained here is indicated both by the fact that the intensity of the absorption band φ is 50% and by the fact that the acidity of the hydroxyl group in position 4 is reduced approximately 2-fold when compared with 4-hydroxyacetophenone.

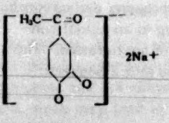


The conjugation of the methoxy group in position 3 with the benzene ring and carbonyl group exerts a bathochromic influence on the absorption band φ, which was not observed in neutral ethanol.

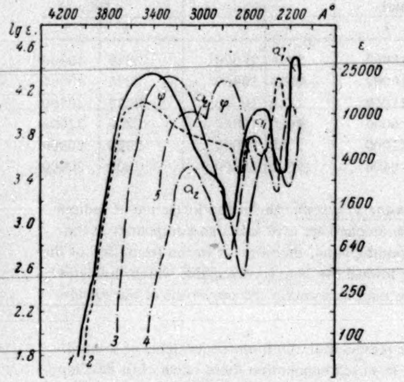
For 3-hydroxy-4-methoxyacetophenone the salt with sodium ethanolate is formed only at the hydroxyl in position 3; here the a_2-band is shifted toward the long waves of the long wavelength region (edge) by 660 A and the maximum is shifted by 380 A (Fig. 4, Curve 1). The φ-band is shifted by only 70 A toward the long wavelengths and is reduced in intensity by 1.8 times when compared with the φ-band in the spectrum of 3-methoxy-4-hydroxyacetophenone in neutral ethanol.

For 3,4-dihydroxyacetophenone the salt-formation proceeds at both hydroxyl groups. Even one mole equivalent of sodium ethanolate in ethanol solution gives a salt, but the latter suffers easy alcoholysis on dilution. 3,4-Dihydroxyacetophenone in ethanol in the presence of 10 and 100 mole equivalents of sodium ethanolate gives a wide φ absorption band with a maximum at λ 3450 A and ε 14000, the intensity of which in the presence of 500 mole equivalents of sodium ethanolate is augmented up to ε 40,000 (Fig. 5, Curves 1, 2 and 3). This band corresponds to the φ-band in the absorption spectrum of 3-methoxy-4-hydroxyacetophenone, but it exceeds it in intensity by 1.8 times. The a_2 absorption band of 3-hydroxy-4-methoxyacetophenone in ethanol in the presence of 500 mole equivalents of sodium ethanolate has the same position (λ 3460 A and ε 10000) and, being less intense, is masked by the more intense φ-band, forming an expansion in its lower portion.





3,4-Dihydroxyacetophenone and its methyl ethers in concentrated sulfuric acid. 3,4-Dihydroxyacetophenone and its isomeric monomethyl ethers were studied in concentrated sulfuric acid (d 1.84) at concentrations of $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$M. Yellow-colored solutions were obtained. To check for the absence of sulfonation the solutions were diluted 10-fold and the absorption spectra of the substances were taken in dilute sulfuric acid; the spectra obtained here are very close to the spectra obtained in water.



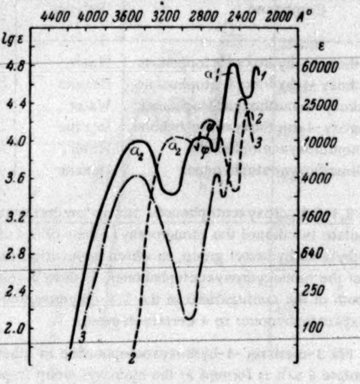


Fig. 3. 1) 3-Methoxy-4-hydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M. + 100 mol. $NaOC_2H_5$, 2) 3-methoxy-4-hydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M. + 10 mol. $NaOC_2H_5$, 3) 4-hydroxyacetophenone in ethanol $10^{-3} - 5 \cdot 10^{-5}$ M. + 10 mol. $NaOC_2H_5$, 4) 3-methoxyacetophenone in ethanol $10^{-3} - 6 \cdot 10^{-5}$ M., 5) 3-methoxy-4-hydroxyacetophenone in ethanol $2 \cdot 10^{-3} - 10^{-5}$ M..

Fig. 4. 1) 3-hydroxy-4-methoxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M. + 500 mol. $NaOC_2H_5$, 2) 3-hydroxy-4-methoxyacetophenone in ethanol $2 \cdot 10^{-3} - 2 \cdot 10^{-5}$ M., 3) 3-hydroxyacetophenone in ethanol $10^{-3} - 2 \cdot 10^{-5}$ M. + 100 mol. $NaOC_2H_5$.

The absorption spectra of 3,4-dihydroxyacetophenone and its isomeric monomethyl ethers in concentrated sulfuric acid solutions, due to the great polarizing influence of the latter, give strongly developed φ bands, characterized by great width and absorption intensity.

The general character of their absorption spectra curves corresponds to the absorption spectra of the 4-hydroxy and 4-methoxyacetophenones in concentrated sulfuric acid, but they are shifted toward the long wavelengths by 110-150 A and are characterized by an intensity that is 3.6, 1.6 and 3.3 times greater, respectively (Table 3).

The conjugation of the hydroxyl group in position 3 with the benzene ring and carbonyl group appears as a strongly bathochromic effect, being expressed in the shifting of the long-wave edge of the φ band of 3,4-dihydroxyacetophenone and its monomethyl ethers by 400-500 A toward the long wavelengths, and also in a hypsochromic effect, expressed in a heightening of the absorption band intensity. Here the greatest increase in the intensity of the φ band is reached for the 3-methoxy-4-hydroxyacetophenone (ε 100,000) and for the 3,4-dihydroxyacetophenone (ε 90,000), while for 3-hydroxy-4-methoxyacetophenone the intensity reaches a value of only ε 45,000, i.e. it is 2.2 times less, which shows the role played by the free hydroxyl group in increasing conjugation and the growth in the intensity of the φ band. The yellow color of the solutions of 3,4-dihydroxyacetophenone and its monomethyl ethers in concentrated sulfuric acid can indicate the formation of the carbonium salt with the carbon of the carbonyl group.

Discussion of the Absorption Spectra of 3,4-Dihydroxyacetophenone and Its Methyl Ethers

In 1915 Auwers [7] studied the influence of position isomerism in aromatic aldehydes, ketones and esters on the molecular refraction, and to explain the greater molecular exaltations shown by benzene derivatives he assumed a transition from the neutral conjugation of the double bonds in the benzene ring to an actual conjugated system with participation of the substituent groups as a function of their degree of unsaturation. The hydroxyl group gives a very strong increase in molecular exaltation when it is introduced into a benzene

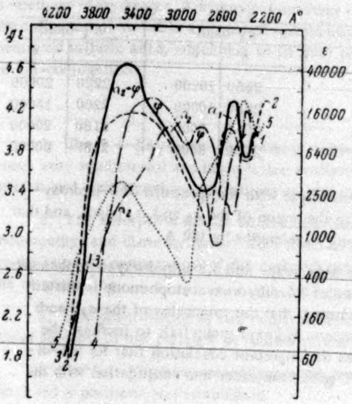


Fig. 5. 1) 3,4-dihydroxyacetophenone in ethanol $2\cdot10^{-3}-2\cdot10^{-5}$ M. + 500 mol. $NaOC_2H_5$, 2) 3,4-dihydroxyacetophenone in ethanol $2\cdot10^{-3}-2\cdot10^{-5}$ M. + 100 mol. or 10 mol. $NaOC_2H_5$, 3) 3,4-dihydroxyacetophenone in ethanol $2\cdot10^{-3}-2\cdot10^{-5}$ M. + 1 mol. $NaOC_2H_5$, 4) 4-hydroxyacetophenone in ethanol $2\cdot10^{-3}-2\cdot10^{-5}$ M. + 1000 mol. $NaOC_2H_5$, 5) 3-hydroxyacetophenone in ethanol $2\cdot10^{-3}-2\cdot10^{-5}$ M. + 1000 mol. $NaOC_2H_5$.

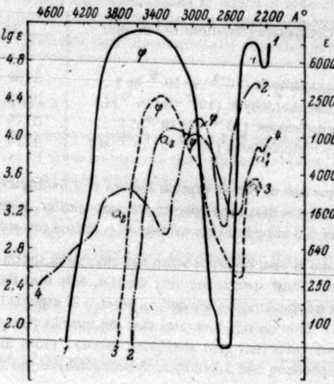


Fig. 6. 1) 3-Methoxy-4-hydroxyacetophenone in conc. H_2SO_4 $2\cdot10^{-3}-2\cdot10^{-5}$ M., 2) 3-methoxy-4-hydroxyacetophenone in 9.5% H_2SO_4 $2\cdot10^{-3}-2\cdot10^{-5}$ M., 3) 4-hydroxyacetophenone in 63.8% H_2SO_4 $10^{-2}-2\cdot10^{-5}$ M., 4) 3-methoxyacetophenone in conc. H_2SO_4 $10^{-3}-10^{-4}$ M.

derivative, already possessing actual conjugation, like the aromatic aldehydes, ketones and esters.

Auwers also made similar molecular refraction studies for the aliphatic compounds and came to the conclusion that for aromatic compounds there exists a grouping of ring bonds that is similar to the substituent bonds. Auwers studied the isomeric hydroxybenzaldehydes. His data went parallel with the spectrographic study data for the hydroxybenzaldehydes and were used by N. A. Valyashko [8] in studying the dihydroxybenzaldehydes, and later together with coworkers – the hydroxy- and dihydroxyacetophenones for the purpose of elucidating the spectrographic study results.

TABLE 3

Compound (In Concentrated Sulfuric Acid, d 1.84)	φ-band		a_1-band	
	λ	ε	λ	ε
3-Methoxy-4-hydroxyacetophenone	3500	100000	2350	100000
3,4-Dihydroxyacetophenone	3400	90000	2370	100000
3-Hydroxy-4-methoxyacetophenone	3500	45000	2340	20000

According to Auwers, in actual conjugations the hydroxyl group, entering into conjugation with the double bonds of the benzene ring, behaves like an unsaturated group with residual affinities. According to A. N. Nesmeyanov [9], in many organic compounds the aromatic systems behave like systems of conjugated bonds, in which connection the unshared pair of electrons of the O, N and other atoms can play the role of the π-pair of electrons for the second double bond of the conjugated system.

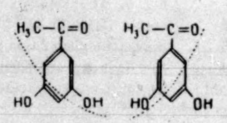
In 1938 N. A. Valyashko and M. M. Shcherbak [10] made a spectrographic study of 3-hydroxybenzaldehyde and 3,5-dihydroxybenzaldehyde, while N. A. Valyashko and A. E. Lutsky [11] made a similar study of 3-hydroxyacetophenone and 3,5-dihydroxyacetophenone. The spectrographic study data of these authors are shown in Table 4, since they lead to some important conclusions.

TABLE 4

Compound (Solutions in Ethanol)	a_2-band		a_1-band		a'_1-band	
	λ	ε	λ	ε	λ	ε
3-Hydroxybenzaldehyde ($10^{-3}-2\cdot10^{-5}$ M.)	3180	3500	2550	10000	2220	20000
3,5-Dihydroxybenzaldehyde ($10^{-1}-2\cdot10^{-5}$ M.)	3340	3500	2550	10000	2200	15000
3-Hydroxyacetophenone ($10^{-3}-2\cdot10^{-5}$ M.)	3110	4000	2525	9000	2180	20000
3,5-Dihydroxyacetophenone ($10^{-2}-2\cdot10^{-5}$ M.)	3210	4000	2650	8000	2180	20000

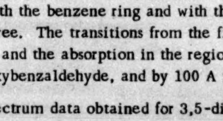
A comparison of the absorption spectra of 3,5-dihydroxybenzaldehyde with the spectrum of 3-hydroxybenzaldehyde shows that their spectra are very similar, especially in the region of the a_2 and a_1 bands, and that the a_2 band of 3,5-dihydroxybenzaldehyde is shifted towards the long wavelengths by 160 A.

The same is also observed when the absorption spectra of the 3-hydroxy- and 3,5-dihydroxyacetophenones are compared. Their spectra are very similar, only that the a_2 band of 3,5-dihydroxyacetophenone is shifted by 100 A toward the long wavelengths. What is of especial importance is that the intensities of the a_2 bands are the same. This clearly indicates that the introduction of the second hydroxyl group fails to increase the number of molecules that give absorption spectra. From this ensues the important conclusion that for 3,5-dihydroxyacetophenone and 3,5-dihydroxybenzaldehyde the carbonyl group can enter into conjugation with the benzene ring with only one hydroxyl group:



But since both of the hydroxyl groups are equal in value, then it is necessary to assume that the conjugation of the carbonyl group with the benzene ring and with the hydroxyl groups in the 3 and 5 positions proceeds separately to the same degree. The transitions from the first structure to the second and the reverse reduce the vibration frequencies, and the absorption in the region of the a_2 band is shifted toward the long wavelengths by 160 A for 3,5-dihydroxybenzaldehyde, and by 100 A for 3,5-dihydroxyacetophenone.

Applying the absorption spectrum data obtained for 3,5-dihydroxyacetophenone to the absorption spectrum of 3,4-dihydroxyacetophenone, we assume that in this molecule also there occurs separate conjugation of the carbonyl group with the benzene ring and with one of the two hydroxyl groups — either in position 3 or 4.



m-conjugation (1,3) p-conjugation(1,4)

Based on energy considerations both of the conjugations are quite close to each other: 1,3-, 95 kcal/mol., 1,4-, 106 kcal/mol. (position of the absorption bands a_2 λ 3070 A and φ λ 2760 A) [12].

For o- and p-substitution of chromophore and auxochrome groups, in the given case the carbonyl and hydroxy groups, conjugation leads to o- and p-quinoid structures. Apparently, the conjugation of these groups in the m-position should be regarded as being a cross conjugation of two conjugated systems of bonds, as is shown in the presented diagram for 1,3-conjugation. Here the double bond is found in conjugation with the carbonyl group, the same as in o-conjugation, which agrees with the fact that the spectrum of the m-derivative coincides with the spectrum of the o-substituted derivative, but differs somewhat in showing a lower absorption band intensity. This phenomenon of two conjugations of the carbonyl group with the benzene ring and with one of the two hydroxyl groups in the 3 and 4 positions is retained in the molecules of 3,4-dihydroxyacetophenone, 3-methoxy-4-hydroxy-, 3-hydroxy-4-methoxy- and 3,4-dimethoxyacetophenones in different solvents, under the influence of variable amounts of sodium alcoholates in the formation of salts and when dissolved in concentrated sulfuric acid, which due to its great polarizing influence facilitates especially powerful development of 1,4-conjugation.

SUMMARY

1. The 3,4-dihydroxy-, 3-methoxy-4-hydroxy-, 3-hydroxy-4-methoxy- and 3,4-dimethoxyacetophenones were synthesized and the solution absorption spectra of these compounds were studied in water, ethanol, hexane and dichloroethane, in sodium ethanolate solutions and in concentrated sulfuric acid.

2. The absorption spectra in the ultraviolet region for 3,4-dihydroxyacetophenone and its isomeric monomethyl and dimethyl ethers were found to be complex and corresponding to the absorption determined by the separate conjugations of the carbonyl group and the 3- and 4-hydroxy- and methoxy- groups with the benzene ring.

3. The phenomenon of two conjugations of the 1,3 and 1,4 type is quite stable and is retained in different solvents in the presence of sodium ethanolate and in concentrated sulfuric acid solution.

4. For 3,4-dihydroxyacetophenone the presence of a hydrogen bond between the hydroxyl groups in the 3 and 4 positions was established.

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* T.p. = C. B. Translation pagination.

DERIVATIVES OF 4-HYDROXY- AND 4-BUTOXY-5,6,7,8-TETRAHYDRONAPHTHALENE-2-CARBOXYLIC ACIDS

S. I. Sergievskaya and E. G. Popova

In their searches for new anesthetic agents different investigators have prepared the alkamino esters of hydroxy and alkoxy acids of the benzene and naphthalene series [1-6]; among the compounds prepared here the most interesting in their anesthetic action proved to be the alkamino esters of some of the acids with a butoxy group in the ring.

The alkamino esters of hydroxy and alkoxy acids in the tetrahydronaphthalene series have not been known up to now. In this paper we describe the 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid, its acid chloride and two of its dialkylaminoalkyl esters.

The hydrochlorides of the alkamino esters of 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid are crystalline substances, the water solutions of which show neutral to litmus.

In addition to the above mentioned butoxy acid derivatives, we prepared the following derivatives of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid: the methyl, ethyl and isoamyl esters, the hydrazide and the acetyl derivative.

EXPERIMENTAL

Methyl ester of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 12 g of hydroxy acid was dissolved in 120 ml methyl alcohol, 6 ml concentrated sulfuric acid was added to the solution which was then saturated with hydrogen chloride until 10% addition in weight and then boiled for 12 hours. Methyl alcohol was driven off in vacuum and the residue was mixed with water; the precipitate that formed was washed with water, with a sodium carbonate solution, and again with water. Yield 12.4 g (96%). The product was recrystallized from a mixture of benzene and petroleum ether. It was colorless, m.p. 127.5-128.5°, soluble in methyl alcohol, ethyl acetate, dichloroethane, ether, acetone, and with heating – in benzene, not soluble in petroleum ether.

Found %: C 69.78; H 6.70. $C_{12}H_{14}O_3$. Calculated %: C 69.88; H 6.84.

4-Acetylhydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. A mixture of 1.4 g hydroxy acid and 0.83 g of acetic anhydride with a small quantity of sulfuric acid was heated on a water bath for 4 hours; recrystallization was from benzene. The product was a colorless substance, m.p. 180-181°; readily soluble in acetone, ethyl acetate and ethyl alcohol.

Found %: C 66.71; H 5.99. $C_{13}H_{14}O_4$. Calculated %: C 66.65; H 6.02.

Methyl ester of 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 10 g methyl ester of the hydroxy acid was dissolved in 10 ml methylethyl ketone with heating; 6.7 g of powdered potash and 9 g of butyl iodide were added to the solution and the mixture was boiled for 10 hours with stirring. The precipitate was filtered off and washed with methylethyl ketone. Methylethyl ketone was driven off in vacuum from the filtrate on a boiling water bath. The residue was mixed with petroleum ether and after cooling, the initial substance – the methyl ester of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (m.p. 125°, 1 g) crystallized and was filtered off. Petroleum ether was driven off from the filtrate and the oily residue was mixed with a small quantity of methyl alcohol and cooled; crystallization took place and the precipitate which formed was filtered off and washed with methyl alcohol. Yield 8g (70%, on the basis initial methyl ester taken for reaction). The methyl ester of ar-4-butoxytetrahydronaphthalene-2-carboxylic acid was a colorless crystalline substance, m.p. 49-50° (from methyl alcohol), readily soluble in ether, petroleum ether, ethyl acetate, benzene, acetone, somewhat less soluble in methyl and ethyl alcohols.

Found %: C 73.12; H 8.20. $C_{16}H_{22}O_3$. Calculated %: C 73.25; H 8.45.

4-Butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. A mixture of 6g of methyl ester of the butoxy acid and 11.5 ml of 2 N alcoholic solution of caustic potash was boiled for 8 hours. After the usual treatment, we obtained 4.7 g (82%) of product. After recrystallization from a mixture of petroleum ether and benzene, it was a colorless substance, m.p. 166-167°; the acid was soluble in methyl and ethyl alcohols, benzene, ethyl acetate, dichloroethane, ether and difficultly soluble in boiling petroleum ether.

Found %: C 72.25; H 8.13. $C_{15}H_{20}O_3$. Calculated %: C 72.55; H 8.12.

Chloride of 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. A mixture of 3.6 g of butoxy acid and 9 g thionyl chloride was boiled for 8 hours; the thionyl chloride was driven off in vacuum; the residue was distilled, b.p. 180-182° at 5 mm. Yield 3.2 g (84%). It was an almost colorless substance, m.p. 47.5-48.5°, soluble in ether, benzene, ethyl acetate and petroleum ether.

Found %: Cl 13.46. $C_{15}H_{19}O_2Cl$. Calculated %: Cl 13.29.

β-Diethylaminoethyl ester of 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (hydrochloride). 1.5 g of the butoxy acid chloride was dissolved in 1.5 ml benzene and 0.66 g of diethylaminoethanol was gradually added with stirring and the reaction mixture was then boiled for 30 minutes with stirring. After cooling, the precipitate was filtered off, washed with benzene and recrystallized several times from a mixture of ethyl acetate and acetone. It was a colorless substance, m.p. 148.5-149.5°. It was readily soluble in ethyl alcohol, soluble in acetone, upon heating — in ethyl acetate and benzene, and insoluble in ether. Its solubility in distilled water was approximately 1 : 20 parts (ester : water).

Found %: C 65.63; H 8.88; N 3.75. $C_{21}H_{34}O_3NCl$. Calculated %: C 65.69; H 8.92; N 3.65.

β-Dimethylaminoethyl ester of 4-butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (hydrochloride).

It was prepared by the same method used for the preparation of the β-diethylaminoethyl ester. After repeated crystallizations from a mixture of ethyl acetate and acetone (2 : 1), the substance melted at 125-126°. It was soluble in ethyl alcohol, with heating — in benzene and ethyl acetate, and insoluble in petroleum ether. Its solubility in distilled water was approximately 1 : 20.

Found %: C 64.23; H 8.31; N 3.93. $C_{19}H_{30}O_3NCl$. Calculated %: C 64.12; H 8.50; N 3.94.

Ethyl ester of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 3 g of the hydroxy acid was dissolved in 30 ml of anhydrous ethyl alcohol, 1.5 ml of concentrated sulfuric acid was added and the reaction mixture was saturated with hydrogen chloride until 10% weight addition and then boiled for 10 hours. Further treatment was the same for the preparation of the methyl ester. Yield 3.2 g (94%). After recrystallization from a mixture of petroleum ether and dichloroethane, the product was a colorless substance, m.p. 110-111°. It was soluble in methyl alcohol, ether, benzene, dichloroethane and insoluble in petroleum ether.

Found %: C 71.03; H 7.25. $C_{13}H_{16}O_3$. Calculated %: C 70.88; H 7.32.

Hydrazide of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. 2.8 g of ethyl ester of the hydroxy acid was dissolved upon heating in 1.5 ml of anhydrous ethyl alcohol, 1.5 g of hydrazine hydrate was added and the reaction mixture was heated over a boiling water bath for 7 hours. Yield 1.9 g (72%) of product. After recrystallization from a mixture of ethyl alcohol and petroleum ether, it was a colorless substance which melted at 211-213°. It was soluble with heating in methyl and ethyl alcohols, insoluble in petroleum ether and benzene, and difficultly soluble with heating in water.

Found %: N 13.72. $C_{11}H_{14}O_2N_2$. Calculated %: N 13.58.

Isoamyl ester of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid. A mixture of 3 g of the hydroxy acid, 30 ml isoamyl alcohol and 1.5 ml concentrated sulfuric acid was boiled for 6 hours. After suitable treatment, the product was distilled, boiled at 206-208° (4 mm) and slowly crystallized upon cooling. It was a faintly yellowish substance which melted at 57-59°. It was readily soluble in ordinary organic solvents.

Found %: C 72.93; H 8.14. $C_{16}H_{22}O_3$. Calculated %: C 73.25; H 8.45.

SUMMARY

4-Butoxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid and some of its alkylaminoalkyl esters and other derivatives were prepared, and also some derivatives of 4-hydroxy-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid.

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MECHANISM FOR THE CLEAVAGE OF ARYLSULFONYLGLYCINES AND THEIR N-DERIVATIVES

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Earlier one of us had established [1] that the heating of arylsulfonylglycines and their N-derivatives with aqueous ammonia leads to the formation of thiophenols, carbon dioxide and amines in accord with the equation:

$$ArSO_2NRCH_2COOH \longrightarrow ArSH + RNH_2 + 2CO_2. \qquad (I)$$

Further studies of this reaction [2] revealed that the methyl ethers of thiophenols are formed if the ammonia is replaced by methylamine. The thio ethers are formed as the result of the secondary reaction:

$$ArSH + CH_3NH_2 \longrightarrow ArSCH_3 + NH_3. \qquad (II)$$

We postulated that the first intermediate product in Reaction (I) is the sulfinate ion, formed in the rupture of the arylsulfonylglycine molecule at the S−N bond. A similar viewpoint was expressed by Wiley and Smith, who observed the formation of diphenyl disulfide and carbon dioxide in the decarboxylation of α-(benzenesulfamino)propionic acid in pyridine in the presence of acetic anhydride [3].

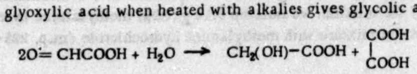
Taking into consideration the stability of the sulfinate ion in strongly alkaline medium, we decided to study the reaction of the arylsulfonylglycines with caustic alkalies. It was revealed that when the arylsulfonylglycines are heated up to 240° with 0.5 N sodium hydroxide solution that they actually do suffer cleavage with the formation of arylsulfinic acids, which we isolated either in the free form or, using the method of Thomas [4], as the iron salt. In addition, ammonia (methylamine in the case of p-toluenesulfonylsarcosine) and oxalic acid were isolated from the reaction mixture.

This makes it possible to assert that the cleavage of arylsulfonylglycines in alkaline medium proceeds through the stage of forming the sulfinic acid ion:

$$ArSO_2{-}NR{-}CH_2COO^- \longrightarrow ArSO_2^- + R\overset{+}{N}CH_2COO^- \qquad (III)$$

$$R\overset{+}{N}CH_2COO^- \xrightarrow[-H^+]{} RN{=}CHCOO^- \xrightarrow{+H_2O} RNH_2 + O{=}CHCOO^-. \qquad (IV)$$

As is known [5], glyoxylic acid when heated with alkalies gives glycolic and oxalic acids:



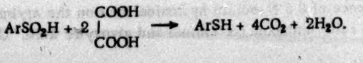
(V)

$$2O{=}CHCOOH + H_2O \longrightarrow CH_2(OH){-}COOH + \begin{array}{l}COOH\\ |\\ COOH\end{array} \qquad (V)$$

There is no basis to assume that the reaction for the cleavage of arylsulfonylglycines with either ammonia or methylamine proceeds by a different scheme; however, in this case the sulfinic acid is reduced by the glyoxylic acid, its imide, or by oxalic acid:

$$ArSO_2H + NH{=}CHCOOH \longrightarrow ArSH + NH_3 + 2CO_2. \qquad (VI)$$

or



(VII)

$$ArSO_2H + 2\begin{array}{l}COOH\\ |\\ COOH\end{array} \longrightarrow ArSH + 4CO_2 + 2H_2O. \qquad (VII)$$

Together with this reaction, in ammonia solution the sulfinic acid suffers partial disproportionation:

$$3\,ArSO_2H \longrightarrow ArSH + 2\,ArSO_3H, \qquad (VIII)$$

$$5\,ArSO_2H \longrightarrow ArSSAr + 3\,ArSO_3H + H_2O. \qquad (IX)$$

Actually, we established that the heating of benzenesulfinic acid with aqueous ammonia solution at 240° gives a mixture of diphenvl disulfide and thiophenol, in an amount not exceeding the yield obtained by the above indicated Reactions (VIII) and (IX) (36.5%).

When benzenesulfinic acid is heated with oxalic acid and ammonia solution under these conditions the sulfinic acid suffers reduction, and the yield of diphenyl disulfide reaches 71%.

EXPERIMENTAL

Experiment 1. A solution of 4 g benzenesulfonylglycine in 120 ml 0.5 N caustic soda was heated in a sealed tube for 6 hours at 240°. After the silicic acid was separated off, the filtrate was divided into two equal portions. In the first half of the filtrate, the ammonia content was determined by distillation, upon addition of concentrated alkali, into a 0.5 N solution of sulfuric acid. We found 0.136 g (86%) ammonia. From the residue, after the ammonia was driven off, treatment with ferric chloride in hydrochloric acid solution yielded 0.96 g (65%) ferric salt of benzenesulfinic acid (68% in another experiment).

For purposes of identification, the ferric salt (0.39 g) was decomposed with ammonia, the ferric hydroxide was filtered off and the filtrate was acidified with hydrochloric acid and extracted with ether. When hydrazine hydrate was added to the ethereal solution, the hydrazine salt of benzenesulfinic acid separated out (0.36 g, 94%) in the form of white flakes, m.p. 127.5° (with decomp.).

Found %: N 9.01, 8.85. $C_{12}H_{16}O_4N_2S_2$. Calculated %: N 8.96.

The literature data [6] gave m.p. 139-141°. In order to ascertain the melting point of the hydrazine salt of benzenesulfinic acid, we prepared the latter from hydrazine hydrate and benzenesulfonic acid. It melted at 128°.

Found %: C 45.78, 45.71; H 4.81, 4.99; N 9.09, 9.01. $C_{12}H_{16}O_4N_2S_2$. Calculated %: C 45.55; H 5.09; N 8.86.

A test mixture of the hydrazine salts of benzenesulfinic acid gave no melting point depression.

When the second half of the reaction liquor was treated with a solution of calcium acetate, 0.63 g (92%) calcium oxalate separated out. The crystalline oxalic acid which was obtained from the prepared oxalate melted at 101-102°. A mixing test with oxalic acid (m.p. 100°) gave no melting point depression.

Experiment 2. 2 g of p-toluenesulfonylsarcosine was heated in a sealed tube for 6 hours at 240° with 60 ml 0.5 N caustic soda solution. The reaction mass was filtered and the filtrate was divided into two equal parts. Upon acidification of half of the filtrate, we isolated 0.55 g of p-toluenesulfinic acid, m.p. 83-84°. The literature data [7] give m.p. 85°. The aniline salt of p-toluenesulfinic acid melted at 116-117°. A mixture test with the aniline salt of p-toluenesulfinic acid (m.p. 118°) gave no melting point depression.

From the second half of the filtrate, upon driving off the methylamine into a solution of hydrochloric acid and subsequent concentration of the solution, we isolated 0.18 g (66%) methylamine hydrochloride, m.p. 226-228° (from absolute alcohol). A test mixture with methylamine hydrochloride (m.p. 225-226°) gave no melting point depression.

Experiment 3. A mixture of 2 g benzenesulfinic acid, 1.5 g oxalic acid and 20 ml of 6% ammonia was heated in a sealed tube for 6 hours at 240°. After opening the tube, the reaction mixture was oxidized by having air blown through it. We isolated 0.91 g (71.5%) diphenyldisulfide, m.p. 55-57°. A text mixture with diphenyldisulfide (m.p. 58-59°) gave no melting point depression.

SUMMARY

The mechanism for the cleavage of arylsulfonylglycines and their N-derivatives when heated in alkaline medium was established. Under the influence of 0.5 N sodium hydroxide solution the arylsulfonylglycines are cleaved with the formation of the sulfinic acid, ammonia (or amine) and glyoxylic acid. Under conditions of

lower alkalinity (ammonia) the sulfinic acid is reduced by the glyoxylic acid and its transformation products into aromatic disulfides and mercaptans.

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THE CHEMISTRY OF HETEROCYCLES*

XXIII. THE SYNTHESIS OF 9-PHENYLACRIDINE BASED ON 2-AMINOTRIPHENYLCARBINOL AND THE MECHANISM OF THIS TRANSFORMATION

P. A. Petyunin, N. G. Panferova and M. E. Konshin

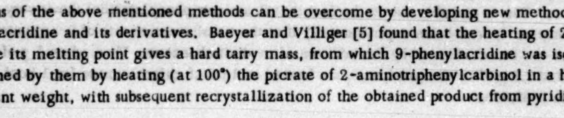
The 9-phenylacridine derivatives have found extensive use as dyestuffs [1]. 9-Phenylacridine itself is used for the protection of aluminum from the corrosion caused by weak hydrochloric acid [2]. 9-Phenylacridine is usually obtained by heating diphenylamine with benzoic acid in the presence of zinc chloride [3]. However, this method proves to be inconvenient when the reaction is run with diphenylamine derivatives that have meta-substituents, since in this case a mixture of isomers is obtained. Organomagnesium and organolithium compounds have been used to obtain 9-phenylacridine and its derivatives [4]. Because of the low yields or the difficult availability of the starting materials the organometal synthesis method has failed to receive extensive use.

The limitations of the above mentioned methods can be overcome by developing new methods for the preparation of 9-phenylacridine and its derivatives. Baeyer and Villiger [5] found that the heating of 2-aminotriphenylcarbinol above its melting point gives a hard tarry mass, from which 9-phenylacridine was isolated. The latter was also obtained by them by heating (at 100°) the picrate of 2-aminotriphenylcarbinol in a hydrogen atmosphere to constant weight, with subsequent recrystallization of the obtained product from pyridine.

In both cases the yields of 9-phenylacridine were not indicated, and consequently the performed experiments bear a qualitative character.

The objectives of the present study were to develop a synthesis method for the preparation of 9-phenylacridine, based on 2-aminotriphenylcarbinol, and to consider the mechanism of this transformation. It is known that triphenylcarbinol contains a labile hydroxyl group and easily reacts with acids [6] and with malonic ester [7]. The mobility of the hydroxyl group is raised considerably if electron-donor substituents are introduced into the phenyl radicals. Thus, the free crystal violet base condenses easily with aliphatic aldehydes and nitro compounds [8], 4,4'-tetramethyldiaminotriphenylcarbinol condenses with 1-phenyl-3-methyl-5-pyrazolone [9], etc.

Taking into consideration the presence of an extremely labile hydroxyl group in triphenylcarbinol and its derivatives, the mechanism for the transformation of 2-aminotriphenylcarbinol (I) into 9-phenylacridine (II) can be depicted as follows:



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[*] The previous communications were published under the title of "N-Arylamides of Hydroxy Carboxylic Acids and Their Transformation Into Heterocyclic Compounds".

TABLE 1

Time of heating (minutes)	Yield (%)
120	86.30
60	97.08
30	94.90
10	90.60
5	87.37

Remarks: In all cases the experiments were run with 1 g of 2-aminotriphenylcarbinol in 10 ml of nitrobenzene. A small amount of tar was formed when the reaction mass was heated for 2 hours.

TABLE 2

Amount of nitrobenzene (ml.)	Yield (%)
10	87.37
5	94.90
1	93.85

Remarks: The experiments were run with 1 g of 2-aminotriphenylcarbinol; the time of heating was 5 minutes.

If the representations that the ionic mechanism prevails for the indicated reaction are correct, then it can be expected that closure of the acridine ring in 2-aminotriphenylcarbinol can also be effected by running the experiments in polar solvents, since it it known that triphenylcarbinol derivatives suffer dissociation in the latter [10]. Our experiments confirmed this postulation. Both nitrobenzene and chlorobenzene were used as reaction media, in which connection the best results were obtained when the experiments were run in nitrobenzene.

The influence of the time of heating (Table 1) and the amount of nitrobenzene (Table 2) on the yield of 9-phenylacridine was studied.

From the presented data it can be seen that to complete the reaction and obtain high yields of 9-phenylacridine it is sufficient to heat the reaction mass for 5 minutes and to use a nitrobenzene to 2-aminotriphenylcarbinol ratio of 1 : 1.

In chlorobenzene an appreciable amount of 9-phenylacridine is formed only after the reaction mass is heated for 5 hours. This is probably due to the fact that 2-aminotriphenylcarbinol shows very slight dissociation in chlorobenzene. It was shown experimentally that the transformation rate of 2-aminotriphenylcarbinol in chlorobenzene can be accelerated by the addition of m-dinitrobenzene. Thus, when 1 g of 2-aminotriphenylcarbinol and 1.8 g of m-dinitrobenzene are heated in 3 ml of chlorobenzene for 1 hour the yield of 9-phenylacridine is 93.85%.

EXPERIMENTAL

A solution of 1 g 2-aminotriphenylcarbinol in 1 ml nitrobenzene was boiled for 5 minutes on a sand bath. After cooling 15 ml 10% hydrochloric acid was added and the nitrobenzene was steam-distilled off. 10% caustic soda solution was added until the solution became alkaline and 9-phenylacridine separated out. It was in the form of needles (from alcohol) with m.p. 184-185.5°; the picrate melted at 227-228°. The literature data for 9-phenylacridine give its melting point as 184° [5]; the picrate had m.p. 227.7° [11].

Yield of product 0.87 g (93.85%).

SUMMARY

Based on 2-aminotriphenylcarbinol, a preparative method for obtaining 9-phenylacridine was developed and the mechanism of this transformation was considered.

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THE REACTION OF A HYDROCHLORIC ACID SOLUTION OF IODINE CHLORIDE WITH BARBITURIC ACID DERIVATIVES

II. BARBITURATES CONTAINING A CYCLOHEXENYL GROUP

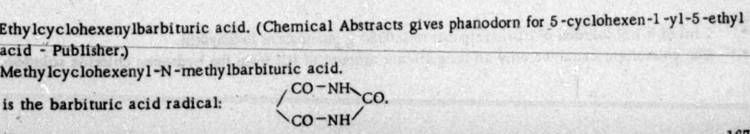
L. I. Rapaport

We failed to find any information in the literature on the reactions of a hydrochloric acid solution of iodine chloride with barbiturates that contain a cyclohexenyl group in their molecule. Some preliminary experiments revealed that when a 0.1N hydrochloric acid solution of iodine chloride is added to a 1% water solution of the sodium salt of either phanodorm* or evipan** that the liquid gradually turns red and a strong iodine odor is released.

When phanodorm is treated with an excess of the hydrochloric acid solution of iodine chloride a copious precipitate is obtained in addition to the formation of iodine. After recrystallization from alcohol a white crystalline powder was obtained, becoming rose-colored on standing, which was very slightly soluble in water and was soluble in alcohol and chloroform; when heated to 168-171° it decomposes with the evolution of iodine vapors. Boiling of the obtained substance with alcoholic KOH solution, followed by acidification of the liquid with nitric acid and the addition of $AgNO_3$, gives a precipitate of silver iodide. The presence of silver chloride in the precipitate could not be shown. Hydrolysis takes place under the influence of dilute mineral acids and iodine is cleaved. On the basis of the iodine content in the obtained substance and taking into consideration the literature data on the hydrolysis of the primary products of iodine chloride addition to unsaturated organic compounds [1-3], we postulated that the substance obtained by us is the iodohydrin of phanodorm, formed as the result of the hydrolysis of the iodochloride derivative. The liberation of iodine, observed when ICl is reacted with phanodorm in hydrochloric acid medium, can be explained as being due to the cleavage of HI when the iodohydrin is hydrolyzed further, which is then oxidized by the iodine chloride. The hydrolysis rate for the iodohydrin increases with temperature elevation.

It is possible that the dihydroxy derivative of phanodorm formed in this manner in comparatively small amounts is soluble in water, which permitted us to obtain the precipitated phanodorm iodohydrin in fairly pure form.

On the basis of these data we postulate that the reaction of phanodorm with a hydrochloric acid solution of ICl proceeds in accord with the following equations:



(1)

$$HI + ICl \rightarrow HCl + I_2. \qquad (2)$$

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* 5,5-Ethylcyclohexenylbarbituric acid. (Chemical Abstracts gives phanodorn for 5-cyclohexen-1-yl-5-ethyl barbituric acid - Publisher.)

** 5,5-Methylcyclohexenyl-N-methylbarbituric acid.

*** = R is the barbituric acid radical:

$$\left\langle \begin{array}{l} CO-NH \\ CO-NH \end{array} \right\rangle CO.$$

The addition product (II) of iodine chloride to the cyclohexenyl double bond, being hydrolyzed in hydrochloric acid medium, first cleaves chlorine (as HCl) to form the iodohydrin (III); then, but at a slower rate, iodine is cleaved and the iodohydrin is converted into the already mentioned dihydroxy derivative (IV). The hydriodic acid that is formed here reacts with the excess ICl, as a result of which iodine is liberated.

The balance for the reaction between phanodorm and a hydrochloric acid solution of iodine chloride confirmed our derived equations.

The experiments made on the isolation of evipan iodohydrin in pure form failed to give positive results, which should be explained as being due to the rapid hydrolysis of the latter at temperatures even as low as 0-5°.

EXPERIMENTAL

Preparation of phanodorm iodohydrin. 0.4 g phanodorm was dissolved in 20 ml 0.1 N NaOH solution and to this solution we added 80 ml 0.1 N hydrochloric acid solution of iodine chloride (2.35 moles ICl to 1 mole of barbiturate). A yellowish precipitate came down, was filtered off and washed with water until the filtrate gave a neutral reaction. The compound was purified by being shaken in alcoholic solution with activated carbon. The solvent was evaporated off at room temperature and the resulting precipitate was dried in a vacuum-desiccator. The iodine content was determined by titration (Volhard) after preliminary boiling of the compound with alcoholic solution of caustic potash.

Found %: I 33.4, 33.2. $C_{12}H_{17}O_4N_2I$. Calculated %: I 33.38.

Balance of the reaction between phanodorm and hydrochloric acid solution of iodine chloride. 0.3054 g weighed out phanodorm was dissolved in 15 ml 0.1 N NaOH solution and to this was added 60 ml 0.1 N ICl solution and the mixture was set aside for 15 minutes.

a) The quantity of iodine which separated out was determined by extraction of the latter with chloroform and titration with 0.1 N $Na_2S_2O_3$ solution, of which 4.70 ml was consumed.

b) After titration with $Na_2S_2O_3$ solution, the chloroform extract was washed with water until a negative reaction for iodine ion was obtained, water was then removed with calcined sodium sulfate and the chloroform was steamed off at 40-50°. After removal of the solvent, the residue was in the form of a white powder with a faint yellowish tint. By iodine content, and by its behavior with solvents and heating it proved identical to the previously prepared phanodorm iodohydrin.

0.3054 g phanodorm yielded 0.3448 g of phanodorm iodohydrin, $C_{12}H_{17}O_4N_2I$. Calculated yield 0.4918 g.

c) Quantity of hydrolyzed phanodorm iodohydrin: as stated above, the quantity of iodine that separated out corresponded to 4.7 ml of 0.1 N solution; therefore, the quantity of HI that reacted with iodine chloride as per Equation (2), was equivalent to 2.35 ml of 0.1 N solution. From these data, we calculated the quantity of hydrolyzed phanodorm iodohydrin*, which proved to be 0.0893 g.

Thus, the total quantity of phanodorm iodohydrin, 0.3448 + 0.0893 = 0.4341 g, amounted to 88.3% of the amount calculated (0.4918 g) for the given weighed portion of phanodorm.

d) The quantity of excess iodine chloride** in the aqueous liquid remaining after the chloroform extraction of iodine, was determined by adding potassium iodide to the liquid and then titrating the iodine ($ICl + KI = KCl + I_2$) with 0.1 N solution of $Na_2S_2O_3$. We thus determined that the quantity of ICl that was consumed by reaction with 0.3054 g of phanodorm was equivalent to 27.9 ml of 0.1 N $Na_2S_2O_3$ solution.

However, we must also allow for that quantity of ICl which reacted with hydriodic acid as per Equation (2), that is, 4.7 ml of 0.1 N solution. Hence, 23.2 ml of 0.1 N ICl was consumed strictly in reaction with phanodorm and amounted to 89.0% of the theoretical amount calculated (25.9 ml) as per Equation (1).

e) The concentration of HCl in the liquid obtained after the iodine chloride had been titrated, was determined by titration with an alkaline solution (the indicator was methyl orange). The difference between the number of milliliters of 0.1 N alkaline solution needed to titrate the same volume of reagent before and after reaction with phanodorm indicated the quantity of HCl that evolved during the reaction as per Equations (1) and (2).*

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* 1 ml of 0.1 N solution of HI corresponds to 0.0380 g phanodorm iodohydrin.

** The chloroform extracted only an insignificant amount of ICl from the hydrogen chloride solution.

For a 0.3054 g weight of phanodorm, this quantity amounted to 13.6 ml of 0.1 N solution. The amount calculated was 27.9 : 2 = 13.95, that is, the amount of HCl found was 97.5% of that calculated.

SUMMARY

1. The reaction of a hydrochloric acid solution of iodine chloride with barbituric acid derivatives, containing the cyclohexenyl group, was studied.

2. Opinions were expressed as to the nature of the reactions that take place here, consisting in the addition of ICl to the double bond of the cyclohexenyl group and in the subsequent hydrolysis of the iodochloride derivative, accompanied by the cleavage of first chlorine, and then of iodine, as HCl and HI.

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* It is necessary to discount, at this point, the number of milliliters of alkaline solution necessary to dissolve the weighed portion of phanodorm.

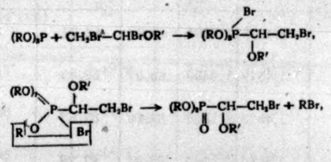
THE MECHANISM OF THE ARBUZOV REARRANGEMENT

II. REACTION OF α,β-DIBROMOETHYL AND α,β-DICHLOROETHYL ISOPROPYL AND α,β-DIBROMOETHYL AND α,β-DICHLOROETHYL BUTYL ETHERS WITH PHOSPHITES

V. S. Abramov and A. P. Pekhman

Earlier [1,2] we had described studying the reaction of α,β-dibromodiethyl ether with phosphites, as a result of which we came to the conclusion that the Arbuzov rearrangement with aliphatic phosphites proceeds in two separately independent stages. Although the intermediate product, formed as the result of the α,β-dibromodiethyl ether adding to the phosphite, was not isolated in chemically pure form, still its presence was conclusively proven on the basis of physical constants and transformations.

In this communication we describe our study of the reaction of the α,β-dibromoethyl isopropyl (I) and α,β-dibromethyl butyl (II) ethers with the ethyl (III) and butyl (IV) esters of phosphorous acid. In these cases also the Arbuzov rearrangement reaction proceeds in two separately independent stages with the formation of the intermediate addition product, which on heating cleaves either propyl bromide or butyl bromide, respectively and is converted into either the ethyl or butyl ester of the α-alkoxy-β-bromoethylphosphinic acid by the sbheme::



$$(RO)_3P + CH_2Br{-}CHBrOR' \longrightarrow (RO)_3\overset{Br}{P}{-}\underset{OR'}{CH}{-}CH_2Br, \qquad (1)$$

$$\longrightarrow (RO)_2\underset{O}{\overset{\|}{P}}{-}\underset{OR'}{CH}{-}CH_2Br + RBr, \qquad (2)$$

where R = C_2H_5 and C_4H_9, R' = iso-C_3H_7 and C_4H_9.

A considerable change in the light refraction index and specific gravity in three to four days, as can be seen from Table 1, indicates formation of the intermediate addition product. The dynamics of the changes in the constants is similar to that described earlier [2]. The almost complete disappearance of the odor of the starting substances also indicates that reaction is taking place.

We also studied the reaction of the α,β-dichloroethyl isopropyl (V) and α,β-dichloroethyl butyl (VI) ethers with the ethyl and butyl esters of phosphorous acid. The reaction of the phosphites with the α,β-dichloroethyl alkyl ethers also probably proceeds with the formation of the intermediate addition product, capable of decomposing into the alkyl halide and the ester of the α-alkoxy-β-chloroethylphosphinic acid when heated, which is also confirmed by the change in the physical constants of the reaction products of the phosphites with the α,β-dichloroethyl alkyl ethers, shown in Table 1. The reaction with the dichloro ethers proceeds at a slower rate and, possibly, fails to go to completion.

The intermediate addition products of the α,β-dibromoethyl alkyl ethers with the phosphites were subjected to thermal decomposition in accord with the second stage of the Arbuzov rearrangement. From the decompositions were obtained the alkyl bromides and the esters of the α-alkoxy-β-bromoethylphosphinic acids, the constants of which are given in Table 2.

TABLE 1

Change in the Physical Constants of the Reaction Mixtures with Time

Reactants	Constants After Mixing		Equilibrium Constants	
	n_D^{20}	d_4^{20}	n_D^{20}	d_4^{20}
I + III	1.4510	1.2509	1.4430	1.2969
II + III	1.4600	1.2443	1.4520	1.2707
I + IV	1.4542	1.1752	1.4485	1.1848
II + IV	1.4559	1.1636	1.4510	1.1808
V + III	1.4250	1.0293	1.4245	1.0367
VI + III	1.4332	1.0296	1.4318	1.0343
V + IV	1.4343	0.9939	1.4337	1.0016
VI + IV	1.4367	0.9811	1.4360	0.9859

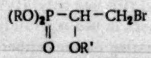
The reaction products of the α,β-dichloroethyl alkyl ethers with the phosphites were also subjected to thermal decomposition. From these decompositions were obtained the corresponding alkyl chlorides and the esters of the α-alkoxy-β-chloroethylphosphinic acids, the constants of which are given in Table 3.

When the addition products of the α,β-dihaloethyl alkyl ethers with the phosphites are reacted with alcohols the corresponding alkyl halides, alcohols and α-alkoxy-β-haloethylphosphinic acid esters are obtained, identical with the esters obtained by thermal decomposition.

The formation of the addition products of the α,β-dihaloethyl alkyl ethers with phosphites is accompanied by a change in volume. We made some quantitative measurements of the volume change in a dilatometer with a graduation fineness of 0.01 ml. The experiments were run at 20°. Prior to mixing, the components were cooled in order to prevent reaction during the mixing. The volume became constant after 3-4 days. The change in the volume of the reaction products was expressed in percents of the original: 1.55 (I + III), 1.04 (I + IV).

TABLE 2

α-Alkoxy-β-bromoethylphosphinic Acid Esters

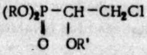


$(RO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OR'}{|}}{CH}-CH_2Br$

R	R'	Boiling Point and Pressure (in mm.)	n_D^{20}	d_4^{20}	MR_D		Yield (%)	Phosphorous Content (%)	
					Found	Calculated		Found	Calculated
CH_2H_5	iso-C_3H_7	130-133° (4)	1.4548	1.2691	64.75	64.21	59.0	9.99, 10.14	10.23
C_2H_5	C_4H_9	125-127 (2)	1.4570	1.2499	69.07	68.83	68.4	9.35, 9.16	9.77
C_4H_9	iso-C_3H_7	173-176 (10)	1.4513	1.1526	83.99	82.68	21.9	8.57, 8.63	8.63
C_4H_9	C_4H_9	182-185 (7)	1.4534	1.1344	88.93	87.29	26.3	8.72, 8.48	8.31

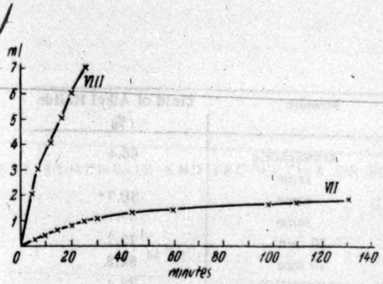
TABLE 3

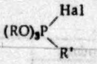
α-Alkoxy-β-chloroethylphosphinic Acid Esters



$(RO)_2\underset{\underset{O}{\|}}{P}-\underset{\underset{OR'}{|}}{CH}-CH_2Cl$

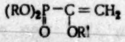
R	R'	Boiling Point and Pressure (in mm.)	n_D^{20}	d_4^{20}	MR_D		Yield (%)	Phosphorous Content (%)	
					Found	Calculated		Found	Calculated
C_2H_5	iso-C_3H_7	138-139° (15)	1.4410	1.1113	61.54	61.31	–	12.15, 12.14	11.97
C_2H_5	C_4H_9	149-151 (11)	1.4418	1.0871	66.29	65.93	26.8	11.69, 11.63	11.38
C_4H_9	iso-C_3H_7	161.5-164 (8)	1.4438	1.0423	80.11	79.78	25.4	9.81, 9.83	9.87
C_4H_9	C_4H_9	180-183 (11)	1.4428	1.0245	84.96	84.30	34.8	9.59, 9.36	9.43



The structure of the intermediate addition product in the Arbuzov rearrangement was not studied. It has been assigned either the covalent structure with pentavalent phosphorus  $(RO)_3P(Hal)R'$ or the phosphonium sturcture $[(RO)_3\overset{+}{P}R']\overset{-}{Hal}$. Landauer and Rudon [3] regard the intermediate compound as being "quasiphosphonium" and call $(PhO)_3PCH_3I$ a "triphenyl methiodide", in this way emphasizing the peculiarity of its structure. Attempting to determine the nature of the phosphorus-iodine bond, they treated the "triphenyl methiodide" with cold silver nitrate solution in anhydrous alcohol and found that the precipitation of silver iodide was slow, and not instantaneous, as in the case of methyltriphenylphosphonium iodide.

In our study we made an attempt to study the reaction for the decomposition of the intermediate addition products obtained by us from α,β-dibromoethyl butyl ether and the triethyl phosphite (VII) and tributyl phosphite (VIII), proceeding in accord with Equation (2). The decomposition of (VII) was run at a bath temperature of 87-90°, and that of (VIII) at 150°. The decomposition rate was determined by the amount of alkyl halide that distilled—ethyl bromide for (VII) and butyl bromide for (VIII). The results of these experiments are given in the figure (above).

TABLE 4

α-Alkoxyvinylphosphinic Acid Esters  $(RO)_2P(=O)-C(OR')=CH_2$

R	R'	Boiling Point and Pressure (in mm)	n_D^{20}	d_4^{20}	MR_D		Yield (%)	Phosphorus Content (%)	
					Found	Calculated		Found	Calculated
C_2H_5	iso-C_3H_7	115-117° (4)	1.4379	1.0462	55.69	55.97	66.5	13.76,13.62	13.96
C_2H_5	C_4H_9	134-136 (5)	1.4430	1.0485	59.67	60.59	37.8	13.29,13.03	13.13
C_4H_9	iso-C_3H_7	162-165 (5)	1.4432	1.0157	72.59	74.44	–	10.99,10.81	11.15

From the experimental data obtained in this manner we calculated the order of the reaction for the decomposition of the intermediate addition product by the substitution method.

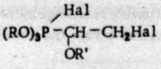
The calculations failed to show definitely whether the reaction was of the first or second order. However, the calculated values that were obtained appear to be more applicable to a first order reaction than they do to a second order reaction. It must be assumed that the covalent structure with pentavalent phosphorus is probably the predominant one for the intermediate addition product.

Treatment of the α-alkoxy-β-haloethylphosphinic acid esters with alcoholic potassium hydroxide solution resulted in hydrogen halide [2, 4] cleavage. Here the α-alkoxyvinylphosphinic acid esters were obtained, the constants of which are given in Table 4.

The studies were made by the earlier described method [2]. Here we will only show the conditions for the thermal decomposition of the intermediate addition products (Table 5).

TABLE 5

Thermal Decomposition of the Addition Products



$$(RO)_3P-\underset{OR'}{\overset{Hal}{CH}}-CH_2Hal$$

Addition Product			Bath Temperature	Pressure	Yield of Alkyl Halide (%)
R	R'	Hal			
C_2H_5	iso-C_3H_7	Br	90-100°	Atmospheric	66.4
C_2H_5	iso-C_3H_7	Cl	80-95	same	–
C_2H_5	C_4H_9	Br	90-100	same	30.7*
C_2H_5	C_4H_9	Cl	90-100	same	–
C_4H_9	iso-C_3H_7	Br	60-90	60 mm	72.7
C_4H_9	iso-C_3H_7	Cl	70-80	70 mm	64.8
C_4H_9	C_4H_9	Br	170	Atmospheric	72.4
C_4H_9	C_4H_9	Cl	120-130	same	59.6

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* The cleavage was completed in vacuo.

SUMMARY

1. It can be assumed that the reaction for the Arbuzov rearrangement of aliphatic phosphites with α,β-dibromoethyl alkyl ethers proceeds with the formation of an intermediate addition product, which when heated cleaves alkyl halide and is converted into an α-alkoxy-β-bromoethylphosphinic acid ester. The reaction proceeds in two separate stages.

The aliphatic phosphites react with α,β-dichloroethyl alkyl ethers, probably, also with the formation of intermediate addition products.

2. Some preliminary considerations on the structure of the intermediate addition product are expressed on the basis of decomposition rate studies.

3. The ethyl and butyl esters of α-isopropoxy- and α-butoxy-β-bromoethyl- and -β-chloroethylphosphinic acids and the ethyl and butyl esters of some α-alkoxyvinylphosphinic acids were prepared.

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* T.p. = C. B. Translation.

THE SYNTHESIS AND PROPERTIES OF SULFAMETHINE – A NEW ANTITUBERCULAR COMPOUND

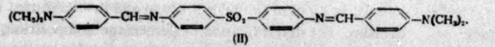
L. M. Kulberg*, S. G. Ryklis, P. A. Yufa and R. P. Veltman

4,4'-Diaminodiphenyl sulfone and some of its derivatives (diasone, promin, promizole, sulphetrone) possess antitubercular activity; however, their use for the treatment of tuberculosis is limited due to their considerable toxicity.

We synthesized a number of 4,4'-diaminodiphenyl sulfone derivatives; their antitubercular activity was studied in the Microbiological Laboratory of the Ukrainian Tuberculosis Institute (by R. O. Drabkina and T. S. Ginzburg). One of these compounds, to which we gave the name of "sulfamethine", proved to be extremely effective in the laboratory treatment of tuberculosis in animals and showed comparatively low toxicity. It was recommended for the treatment of bone-joint tuberculosis and proved to be highly effective as a healing agent, not only stopping the spread of the disease, but also aiding in the restoration of damaged bone tissue.

Sulfamethine (I) is the condensation product of 4,4'-diaminodiphenyl sulfone with p-dimethylaminobenzaldehyde; we obtained it by running the condensation in the presence of sulfuric acid.

I. Kh. Feldman and Z. N. Syrkin [1] described the condensation product of 4,4'-diaminodiphenyl sulfone with p-dimethylaminobenzaldehyde, being the azomethine of structure (II). It was obtained by simply boiling an alcoholic solution of the components:



(II)

Sulfamethine is different from the azomethine: (I) is active against the tubercle bacillus, (II) is inactive; (I) decomposes without melting when heated to 275-280°, (II) has a sharp melting point of 230-231°; solubility in alcohol at room temperature: (I) 0.045%, (II) 0.6%. However, elementary analysis established that the sulfur and nitrogen contents were the same in both compounds, corresponding to the above presented formula; consequently, we assumed that the sulfamethine is a polymer of the azomethine derivative. Such an assumption was confirmed by the fact that azomethine (II) when heated in alcohol in the presence of sulfuric acid is converted into sulfamethine (I).

In comparing the properties of (I) and (II), we established that under the same conditions in acid medium that the azomethine (II) is hydrolyzed more rapidly than is the sulfamethine (I), and its degree of hydrolysis is greater. In neutral medium only the sulfamethine is hydrolyzed. The azomethine fails to react with sodium bisulfite solution, while the sulfamethine under the influence of sodium bisulfite changes from a yellow to a bright orange color. Using the same weight concentrations, the sulfamethine gives a considerably smaller melting point depression for camphor than does the azomethine. X-ray analysis reveals that the azomethine has a well-defined crystalline structure, while the sulfamethine has a diffuse (washed-out) structure, characteristic for high-molecular compounds. On the basis of the obtained data it can be assumed that the sulfamethine is a dimer of the azomethine.

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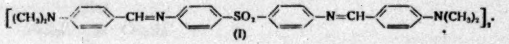
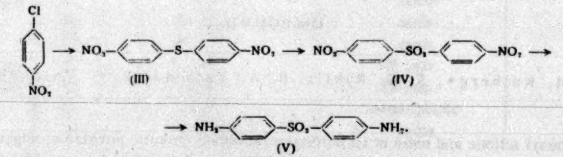
* Deceased.



(I)

EXPERIMENTAL

The initial 4,4'-diaminodiphenyl sulfone (V) was prepared by the following scheme:



4,4'-Dinitrodiphenyl sulfide (III) was prepared by boiling an alcoholic solution of 4-nitrochlorobenzene with sodium disulfide [2]. It was crystallized from glacial acetic acid. Yield 52-54%, m.p. 154-155°.

4,4'-Dinitrodiphenyl sulfone (IV) was prepared by oxidation of (III) with a chromic mixture in glacial acetic acid [3, 4]. It was crystallized from glacial acetic acid or 60% nitric acid. Yield 90%, m.p. 251-252°.

4,4'-Diaminodiphenyl sulfone (V) was prepared from (IV) by reduction with zinc dust in 35% acetic acid. The product was recrystallized from hydrochloric acid solution with ammonia and crystallized from 65% ethyl alcohol. Yield 64%, m.p. 173-174°.

Synthesis of sulfamethine. 20 g 4,4'-diaminodiphenyl sulfone (V) was dissolved with heating in 300 ml alcohol and to this was added a solution of 26 g p-dimethylaminobenzaldehyde in 120 ml alcohol. 18 ml sulfuric acid (d 1.84) was then added drop-wise to the hot reaction mixture with stirring. The dense orange precipitate which came down was carefully rubbed until it congealed. It was filtered, washed with alcohol and then treated with saturated sodium bicarbonate solution •. It was then dried at 60°. Yield 38-40 g. It decomposed when it was heated to 275-280°.

The sulfamethine was a bright yellow powder, tasteless but with a slight honeylike odor. It was very sparingly soluble in water (at 20° – 0.0093%), in alcohol (at 20° – 0.045%) and in ordinary solvents. It inhibited the growth of the tubercle bacillus. For determination of percentage composition, a sample was carefully washed with water to remove admixed sodium bicarbonate and with alcohol to remove possibly admixed free 4,4'-diaminodiphenyl sulfone.

Found %: N 10.94, 10.54; S 6.30, 6.21. $C_{30}H_{30}O_2N_4S$. Calculated %: N 10.98; S 6.27.

Synthesis of azomethine. Azomethine was synthesized by boiling an alcoholic solution of 4,4'-diaminodiphenyl sulfone and p-dimethylaminobenzaldehyde [1]. It melted at 230-231°. The azomethine was in the form of fine yellow needles, slightly soluble in alcohol (at 20° – 0.6%). It did not inhibit the growth of tubercle bacilli.

Conversion of azomethine to sulfamethine. 10 g azomethine was heated with 100 ml alcohol to the boiling point. 4 ml sulfuric acid (d 1.84) was added drop-wise to the hot mass while stirring and the stirring was continued until the reaction mass cooled. It turned orange. Further treatment of the product was the same as for the synthesis of sulfamethine. Yield 9 g. The product did not fuse; when it was heated above 250°, it began to darken and then decomposed. The compound possessed the same antibacterial activity as sulfamethine.

Hydrolysis of sulfamethine and azomethine. a) Hydrolysis in acid medium was performed by the method described in the literature [5]. 0.25 g sulfamethine or azomethine was first washed free of admixed $NaHCO_3$ and (V), and then stirred 2 hours with 100 ml 0.1 N hydrochloric acid at room temperature. Increase in duration

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• Prepared sulfamethine is stored with a 1% admixture of sodium bicarbonate.

and elevation of the temperature of the reaction did not affect the degree of hydrolysis. The latter was determined colorimetrically by the quantity of 4,4'-diaminodiphenyl sulfone (V) which formed.

Preparation of standard solution. The standard was a solution of the dye prepared by coupling diazotized 4,4'-diaminodiphenyl sulfone with an R-acid. Solution 1. 0.124 g of 4,4'-diaminodiphenyl sulfone (0.001 g-equiv.) was diazotized in hydrochloric acid solution by the theoretical quantity of sodium nitrite. Solution 2. 0.6 g R-acid was dissolved in 50 ml of 2% sodium carbonate solution. The solutions were combined. A solution of red dye formed. After 15-20 minutes, the solution was diluted to 250 ml in a volumetric flask with distilled water. The concentration of 4,4'-diaminodiphenyl sulfone in the given standard solution was 1: 2000. It was further diluted as required. Its coloration was maintained upon dilution to $1:10^7$. In the Duboscq colorimeter, it could be used for colorimetric analysis at dilutions of the order of $1:5\cdot10^6$. All solutions had to be prepared with distilled water since the presence of even a small amount of conduit water brought down a precipitate (evidently, an insoluble calcium salt of the dye is formed).

Preparation of a working solution of the substance to be analyzed. The hydrochloride salt of 4,4'-diaminodiphenyl sulfone which formed upon hydrolysis (see above) was diazotized with 0.1 N solution of sodium nitrite and diluted to 250 ml with distilled water. 25 ml of diazo solution was filtered off and coupled with 10 ml 1% solution of R-acid, with addition of 10 ml sodium carbonate solution. After standing 30 minutes the dye solution was diluted to 250 ml. The concentration of the prepared solution, on the basis of the substance to be analyzed, was 1: 10000. The working solution was diluted as required.

Colorimetric analysis. Our most precise results were obtained after dilution of the solution being tested in the range $1:10^5-1:10^6$. Calculation was by formula: $C_X = \frac{C_{st}\cdot H_{st}}{H_X}$, where C_X – concentration of 4,4'-diaminodiphenyl sulfone in the investigated solution after hydrolysis, C_{st} – concentration of 4,4'-diaminodiphenyl sulfone in the standard solution, H_{st} – height of column of standard solution, H_X – height of column of investigated solution.

The percent of hydrolysis was calculated on the basis of colorimetric analysis by formula: $A = \frac{C_X\cdot100\cdot2}{D}$, where A – percent of hydrolysis, D – dilution of the investigated solution on the basis of a weighed portion of investigated substance. Since the molecular weight of the hydrolyzed monomer of azomethine (510) is approximately 2 times as large as the molecular weight of 4,4'-diaminodiphenyl sulfone (248) which formed upon hydrolysis, the right side of the equation was multiplied by 2.

The degree of hydrolysis of sulfamethine proved to be 9.3%, the degree of hydrolysis of azomethine – 33%. This method could be used to determine the content of admixed free 4,4'-diaminodiphenyl sulfone in the prepared compound – sulfamethine; for this purpose, a weighed portion of 1 g of the compound was (without preliminary alcohol washing) steeped in 100 ml of water for 1 hour, with periodic agitation. The liquid was filtered and the content of 4,4'-diaminodiphenyl sulfone in the filtrate was determined as described above. Calculation was by formula:

$$\%\text{DDS}^{\bullet} = \frac{C_{st}\cdot H_{st}\cdot V_X}{H_X\cdot m},$$

where C_{st}, H_{st}, and H_X are explained above; V_X – final volume of investigated solution, m – weighed portion of compound taken.

b) Hydrolysis in neutral medium. 0.2 g of sulfamethine or azomethine was ground in a mortar with water, transferred to a volumetric flask and diluted to 250 ml with distilled water. The suspension was set aside for a long period. At definite intervals, it was filtered, the precipitate was washed with 50 ml of water and the 4,4'-diaminodiphenyl sulfone that formed in the filtrate was determined. Water was again poured over the precipitate on a filter and after some time, a sample was again taken for colorimetric analysis. To determine the effect of temperature on the degree of hydrolysis of the compound in water, it was boiled with the cited quantity of water for 10 minutes, the hot mixture was filtered, the precipitate was washed with hot water and upon cooling, the filtrate was examined as described above. After being steeped in water for 5 days, azomethine hydrolyzed to the extent of 0.1%. The data on the hydrolysis of sulfamethine are given in the table (below).

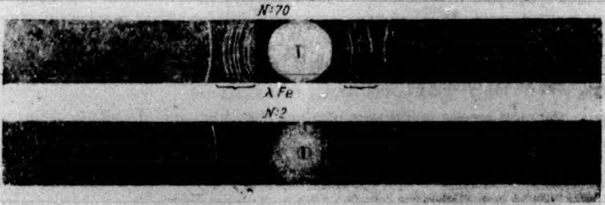
• DDS – diaminodiphenyl sulfone.

Variation in Degree of Hydrolysis of Sulfamethine with Temperature and Duration of Experiment

Temperature	Time (in hours)	Hydrolysis of sulfamethine (in %)
18-20°	2.5	1.1
18-20	24	4.0
18-20	48	7.5
18-20	96	12.5
100	0.17	5.2

It is evident from the data of the table that the degree of hydrolysis of sulfamethine in water is higher, the higher the temperature and the longer the period of interaction (of sulfamethine and water).

Reaction of sulfamethine and azomethine with sodium bisulfite. 2 g sulfamethine or azomethine was steeped in 1.4 g of sodium bisulfite in water for 2 days in a closed container. The azomethine did not change noticeably, even upon subsequent heating. The sulfamethine went from yellow to orange and resinified upon heating.



Debye crystallogram of sulfamethine and azomethine

X-ray analysis. X-ray analysis of the structure of both compounds was carried out under strictly identical conditions by means of a sharp-focus B. Ya. Pines tube. The emission was $K_{\alpha} \cdot Fe$. The wave length was 1.936 A. The current was 1 mA, voltage 22 kV. The illustration shows the crystallograms obtained. The crystallogram of azomethine (No. 70) clearly revealed lines indicating its crystalline structure. * Corresponding lines in the crystallogram (No. 2) were absent or extremely diffuse, in dicating the greater structural complexity of sulfamethine.

SUMMARY

1. A new antitubercular compound, named sulfamethine, was synthesized, which found use in the treatment of bone-joint tuberculosis.

2. Some of the physical and chemical properties of sulfamethine were determined. It was shown that it is a polymer of the azomethine bis-4-(p-dimethylaminobenzalimino)diphenyl sulfone.

3. A method was developed for the colorimetric determination of the degree of hydrolysis for sulfamethine, which method is also suitable for checking on the presence of free 4,4'-diaminodiphenyl sulfone as impurity in the sulfamethine.

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* The parenthetically shaped lines show the diffraction pattern of the substance. The other lines were returned by the collimator.

** T. p. = C. B. Translation pagination.

ALKALOIDS OF *GALANTHUS WORONOVI*

V. ISOLATION OF GALANTHAMIDINE

N. F. Proskurnina and A. P. Yakovleva

While the bulbs of the snowdrop *woronovi* (family *Amaryllidaceae*) have been studied in quite some detail [1], the roots of this plant have not been studied up to now. The pharmacological activity of the alkaloid galanthamine [2], isolated first from the bulbs, and then also from the aboveground portions of the snowdrop, increased the interest toward this plant.

The material used in our study was received from the Transcaucasian Zone Station of the All-Union Institute VILAR in 1951. The roots that were received together with the bulbs had been collected in the Batum region in early December, at the start of the vegetative period.

The alkaloids were extracted from the roots of the snowdrop *woronovi* in the usual manner with dichloroethane. The separation of the alkaloids of this plant (both when working with the bulbs and aboveground portions, and when working with the roots) is made easier by the fact that a portion of the alkaloids shows immediate precipitation when the sulfuric acid extract is made alkaline.

Treatment of the precipitate obtained from the alkaline solution with hot acetone gave, in addition to the alkaloids lycorine and galanthine, also another base in an amount of 0.028%. This base melts at 211-213°, shows optical activity ($[\alpha]_D - 94.2°$), and its analysis is in good agreement with the formula $C_{18}H_{23}O_5N$. In view of the fact that this base is different from all previously described alkaloids, we propose the name of galanthamidine for it. Galanthamidine is quite readily soluble in hot acetone, chloroform and hot methanol, and is difficultly soluble in alcohol and water.

Its reaction with phloroglucinol and conc. H_2SO_4 shows the presence of a methylenedioxy group in galanthamidine. The presence of methoxy groups in galanthamidine could not be shown.

Galanthamidine in chloroform solution in the cold gives a methiodide, which melts at 219° (with decomposition).

As a characteristic of the roots of the snowdrop *woronovi* it should be mentioned that they fail to contain the alkaloid galanthamine, which alkaloid is found to be present in both the bulbs and aboveground portions of this plant.

EXPERIMENTAL

1.5 kg air-dried pulverized roots of the plant was treated with 8% ammonia solution and exhaustively extracted with dichloroethane. The dichloroethane extract was shaken with 5% sulfuric acid. Upon cooling, an excess of ammonia was added to the sulfuric acid solution, after which 8 g of gray precipitate came down from solution during 24 hours of standing.

Isolation of lycorine and galanthine. 8 g bases which came down from ammoniacal solution were boiled two times with acetone, after which 6 g of lycorine, not dissolved in acetone, remained; m.p. 244-246°. From the acetone solution, 0.17 g of galanthine was isolated, m.p. 125-127°.

Isolation of galanthamidine. After the acetone was driven off from the mother liquor, the residue was treated with alcohol, the galanthamidine crystals were filtered off and washed with alcohol. We isolated 0.6 g of base, m.p. 199-202°. After recrystallization from 15 ml methyl alcohol, we isolated 0.35 g galanthamidine, m.p. 211-213°, $[\alpha]_D - 94.2°$ (c = 0.53; l = 1 dm; methanol).

Found %: C 64.63, 64.72; H 6.90, 6.98; N 4.19, 4.25. $C_{18}H_{23}O_5N$. Calculated %: C 64.86; H 6.93; N 4.20.

Galanthamidine methiodide. A small excess of methyl iodide was added to a solution of galanthamidine in chloroform and the liquid was set aside for a day. The crystals that formed upon removal of the solvent were washed with acetone. The methiodide obtained by recrystallization melted at 219° (with decomposition).

SUMMARY

1. The crystalline alkaloid galanthamidine of composition $C_{18}H_{23}O_5N$ and having m.p. 211-213°, $[\alpha]_D - 94.2°$ was isolated from the roots of Galanthus woronovi.

2. Galanthamidine contains the methylenedioxy group. Analysis failed to show the presence of methoxy groups. The nitrogen in galanthamidine is of the tertiary type.

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* T. p. = C. B. Translation pagination.

ALKALOIDS OF THE PLANTS OF THE POPPY FAMILY

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A study of the alkaloidal content of the different types of poppy (Papaveraceae) plants growing in the USSR territory was started many years ago, the chemical study being made by A. P. Orekhov and his coworkers, and the botanical study by P. S. Massagetov. Even in the first paper [1] the alkaloidal content was qualitatively established for the plants: Papaver pavoninum Schrenk., P. nudicaule L., P. armeniacum DC., Glaucium fimbrilligerum B. Fedsch., G. squamigerum Kar. and Kir., Fumaria Vailantii Loisl., Hypecoum pendulum L. In a later paper [2] the alkaloids of the plants Papover armeniacum, P. orientale, P. floribundum, P. bracteatum, Roemeria refracta, Glaucium fimbrilligerum were subjected to a detailed study.

This paper is a continuation of the earlier studies. The alkaloidal content of 11 types of poppy plants was studied; the results that were obtained are given in the table. The following alkaloids are new, for which we propose the names: fumaridine, fumarinine, fumaritine, fumvailine, pagibrine, remeridine and chelidamine. A description of the methods used for the isolation and separation of the alkaloids and the properties of the new alkaloids is given under EXPERIMENTAL; here we will only mention the close similarity of fumaramine and fumaridine. Fumaramine is a yellow substance, $C_{21}H_{22}O_5N_2$, devoid of methoxy groups, contains the CO group (absorption band in the IR-spectrum 1705 cm^{-1}), UV-spectrum: λ_{max} 360 mμ (log ϵ 4.21), 233 mμ (log ϵ 4.60), λ_{min} 315 mμ (log ϵ 3.89), shoulder 250 mμ (log ϵ 4.28). Fumaridine is also a yellow substance, $C_{23}H_{26}O_5N_2$, contains two OCH_3 groups and a CO group (absorption band 1705 cm^{-1}); UV-spectrum is close to that of fumaramine: λ_{max} 350 mμ (log ϵ 4.19), 223 mμ (log ϵ 4.66), λ_{min} 312 mμ (log ϵ 4.00), shoulder 250 mμ (log ϵ 4.35). Apparently, fumaridine is the dimethyl ether of fumaramine.

Study of Plants for Their Alkaloidal Content

Name of plant	Place of gathering the plants	Isolated alkaloids (the percent content in the dry plant is given in parentheses)
Fumaria Schleicheri Soy-Will.	Transcaucasia	Protopine (0.05), fumaridine (0.01), fumaramine (0.01), fumarinine (0.005), fumaritine (0.002), total bases – 0.47%
Fumaria micrantha Lag.	Dagestan	Protopine (0.08, fumaramine (0.01), total bases – 0.6%
Fumaria Vailantii Loisl.	Central Asia	Protopine (0.06), fumaridine (0.005), fumvailine (0.007), total bases – 0.7%
Papaver hybridum L.	Dagestan	Pagibrine (0.03), total bases – 0.12%
Papaver pavoninum Schrenk.	Kirghiz Alatau (steppe)	α-Allocryptopine (0.002), protopine (0.002), remeridine (0.002), total bases – 0.1%
Roemeria hybrida (L.) DC.	Central Asia, Muyun-Kuma	Protopine (0.4), remeridine (0.02), total bases – 0.8%
Glaucium corniculatum (L.) Curt.	Transcaucasia	α-Allocryptopine (0.3), protopine (0.03), total bases – 1%
Glaucium flavum Crantz.	Transcaucasia	Glaucine (0.4), total bases – 2%
Glaucium squamigerum Kar. and Kir.	Central Asia, Tyan-Shan	Protopine (0.5), corydine (corydaline) (1.8), α-allocryptopine (0.2), total bases – 3.6%
Chelidonium majus L.	Altai	Sanguinarine, chelerythrine and chelidamine (0.01), protopine (0.04), chelidonine (0.06)
Hypecoum pendulum L.	Eastern Transcaucasia	Protopine (0.03), total bases – 0.15%

Some of the plants given in the table were studied earlier for their alkaloidal content [3]; in this connection there were isolated: from *P. hibridum*, rheadine $C_{21}H_{21}O_6N$, m.p. 256°; from *G. corniculatum*, protopine; from *G. flavum*, aurotensine (m.p. 128°), isocorydine, glaucine and alkaloid F-47 (m.p. 280°); from *Ch. majus*, chelerythrine, chelidonine, α-homochelidonine, hydroxychelidonine, methoxychelidonine, sanguinarine, α- and β-allocryptopine, protopine and the alkaloid $C_{19}H_{24}ON_2$ (m.p. 198-199°). It can be seen that the material studied by us is different from that studied earlier.

EXPERIMENTAL

I. Alkaloids of Fumaria Schleicheri

1. Isolation of alkaloids. 14 kg dried pulverized plants was steeped in 10% aqueous ammonia solution. The bases were exhaustively extracted with dichloroethane; the bases were transferred from the dichloroethane extract into 10% sulfuric acid and after alkalization of the acidic extract with 25% ammonia solution, were extracted with ether and then with chloroform. Upon evaporation of the ethereal extract to low bulk, we obtained 23 g brown crystalline bases (A), upon evaporation to dryness – 26 g more of a non-crystallized mixture of bases (B). From the chloroform extract, we obtained 17 g dark brown non-crystalline bases. The total alkaloid content was 0.47% of the weight of dry plant.

2. Resolution of total crystalline bases (A). A solution of 23 g bases (A) in 1 liter $CHCl_3$ was chromatographed on 1000 g Al_2O_3. Elution was carried out at first with $CHCl_3$; at this point three zones formed – an upper orange, then a yellow and, finally, a colorless zone, weakly fluorescent in UV-light. The moment the bases appeared in the eluate, elution was continued with a mixture of $CHCl_3$ + 2% CH_3OH. The eluate was collected in portions as the individual zones were displaced. From the colorless zone, we isolated 3 g base which melted at 205-206° from alcohol; its mixture with protopine melted at the same temperature. From the yellow zone, we obtained a mixture of crystalline bases (m.p. 170-190°), from the orange zone – 0.2 g resinous product. The bases from the yellow zone were dissolved in 600 ml $CHCl_3$ and repeatedly chromatographed on 500 g Al_2O_3. Two zones were distinguishable on the column – a yellow upper and a colorless lower zone which fluoresced in UV-light. The bases from the lower zone were eluted with $CHCl_3$, the eluate being collected in 100 ml portions (1-7th fractions). The upper zone was cut into 3 parts, from which the bases were eluted with CH_3OH (8-10th fractions). From Fractions 1-4 we isolated 3 g protopine. From Fractions 6-8, upon mixing the alcoholic solutions of the bases with tartaric acid, we obtained fumaridine tartrate; yield 2 g, m.p. 217° (from 80% alcohol); the salt was difficultly soluble in acetone and in alcohol, more readily in water.

Found %: C 57.37, 57.49; H 5.45, 5.58; N 4.78, 4.72. $C_{23}H_{26}O_5N_2 \cdot C_4H_6O_6$. Calculated %: C 57.85; H 5.75; N 4.99.

Fumaridine – yellow needles, m.p. 190-191° (from methanol); readily soluble in chloroform, less – in methanol, acetone, alcohol and ether; it gave a dark green coloration with Fried's reagent which changed to dark rose and then to brown.

Found %: C 67.05, 67.24; H 6.36, 6.34; N 6.80, 6.83; OCH_3 15.25, 14.93; NCH_3 11.95. M 437 (according to Rast). $C_{23}H_{26}O_5N_2$. Calculated %: C 67.3; H 6.38; N 6.82; $2OCH_3$ 15.12; $2NCH_3$ 14.5. M 410.

After addition of an alcoholic hydrochloric acid solution to a suspension of the base in acetone, we obtained fumaridine hydrochloride, m.p. 213-214° (from alcohol-ether).

Found %: N 6.05, 5.98. $C_{23}H_{26}O_5N_2 \cdot 2HCl$. Calculated %: N 5.79.

Fumaridine picrate was prepared in alcoholic solution, m.p. 204-205°. Fumaridine methiodide formed upon boiling a solution of the base in methanol with an excess of methyl iodide for 3 hours; after crystallization from alcohol it melted at 247-248°.

From Fractions 9 and 10 we isolated fumaramine tartrate, a greenish substance, m.p. 200° (from 50% alcohol); yield 1.2 g. Fumaramine, isolated from the tartrate, was in the form of yellow needles, m.p. 223-224° (from alcohol), poorly soluble in ether, alcohol, acetone and more readily in chloroform.

Found %: C 65.89, 66.14; H 5.66, 5.44; N 7.62, 7.80; NCH_3 11.73; OCH_3 group was not present. M 391 (according to Rast). $C_{21}H_{22}O_5N_2$. Calculated %: C 65.95; H 5.79; N 7.32; $2NCH_3$ 15.18. M 382.

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[*] Yields are given for the substances that were crystalline and had a constant melting point; losses in the mother liquors were not accounted for.

Fumaramine hydrobromide was prepared in alcoholic solution and recrystallized from 75% alcohol; it melted at 258-260°.

Found %: Br 17.36, 17.60. $C_{21}H_{22}O_5N_2 \cdot HBr$. Calculated %: Br 17.21.

3. Resolution of total non-crystalline bases. A solution of 20 g bases (B) in 750 ml $CHCl_3$ was chromatographed on 1000 g Al_2O_3. After washing with chloroform, the sorbate layer was cut into 7 zones of different colors, from which the bases were eluted with CH_3OH (Fractions 1-7). Fractions 3-7 were chromatographed again from $CHCl_3$ solutions on Al_2O_3 (each fraction separately). The colored sorbate columns were cut into parts according to the variation of color of the zones and the bases were eluted with CH_3OH.

From Fraction 4 we isolated 0.78 g of fumarinine oxalate, m.p. 213° (from 25% alcohol). The base isolated from the oxalate was in the form of light yellow needles which melted at 189-190° (from a mixture of chloroform and alcohol), difficultly soluble in acetone and alcohol, more readily – in ether and chloroform. There was a melting point depression when it was mixed with fumaridine.

Found %: C 67.64, 67.71; H 5.33, 5.52; N 4.98, 4.82; NCH_3 7.79; OCH_3 not detected. $C_{16}H_{15}O_4N$. Calculated %: C 67.36; H 5.30; N 4.91; NCH_3 10.18.

Fumarinine hydrochloride melted at 255-257° (from alcohol-ether).

Found %: C 59.96, 60.27; H 5.49, 5.37. $C_{16}H_{15}O_4N \cdot HCl$. Calculated %: C 59.73; H 5.01.

From Fractions 5 and 6 we isolated 0.6 g protopine; from Fraction 7 – 0.3 g protopine and 0.3 g fumaritine in the form of colorless rectangular flakes which melted at 157-159° (from alcohol), readily soluble in acetone, and less – in alcohol and ether.

Found %: C 67.13, 66.98; H 5.47, 5.50; N 3.68, 3.80; NCH_3 8.08. $C_{20}H_{21}O_5N$. Calculated %: C 67.60; H 5.95; N 3.94; NCH_3 8.17.

Fumaritine hydrochloride – colorless rectangular plates, m.p. 224° (from a mixture of alcohol and ether).

Found %: C 60.58, 60.40; H 5.70, 5.49; N 3.59, 3.58. $C_{20}H_{21}O_5N \cdot HCl$. Calculated %: C 61.30; H 5.66; N 3.57.

Fumaritine hydrobromide was obtained in alcoholic solution and recrystallized from alcohol, m.p. 219°.

Chromatographic resolution of the total bases from the chloroform fraction (C) was unsuccessful in isolating the individual substances.

II. Alkaloids of Fumaria Micrantha

15 kg plants was treated as described above. From the ethereal extract we obtained 80 g non-crystalline mixture of brown bases, from the chloroform extract – 15 g of nearly black mass which was not analyzed further. The total alkaloid content was 0.6% of the plant weight.

The bases from the ethereal fraction were rubbed with acetone; a white crystalline substance came down at this point which after crystallization from alcohol, weighed 11 g, m.p. 205-206°; a test mixture with protopine melted at the same temperature. The bases from the mother liquors were dissolved in 300 ml $CHCl_3$ after isolation of protopine and then shaken with 5% NaOH, free of phenolic bases. We obtained 56 g non-phenolic bases and 10 g phenolic bases; there was no crystallization.

A solution of 56 g non-phenolic bases in 1000 ml $CHCl_3$ was chromatographed on 1000 g Al_2O_3. $CHCl_3$ was used for elution (1-16th fractions), $CHCl_3$ + 2% CH_3OH (17-28th fractions) and CH_3OH (29th fraction). 50 ml of eluate was collected from each fraction. The bases from each fraction were rubbed with methanol; there was crystallization in the 1-11th and 17-20th fractions. From the crystalline bases of the 1-3rd fractions (0.2 g) in alcoholic solution, we obtained an oxalate (0.15 g) from which we isolated a base, m.p. 209-210° (from alcohol). From the crystalline bases of the 4-11th fractions (1.9 g) in alcoholic solution, we obtained an oxalate, m.p. 230°, from which we isolated protopine. From the 19-20th fractions we obtained 0.35 g base, m.p. 222-223° (from alcohol); a mixture with fumaramine gave no melting point depression. From Fractions 17-18 and from the mother liquors, after separation of fumaramine from Fractions 19-20, we obtained 0.95 g of a hydrobromide, m.p. 258-260° (from 50% alcohol). The base, after isolation from the hydrobromide, proved identical to fumaramine.

III. Alkaloids of Fumaria Vaillantii

6 kg of plants was treated as described above. From the ethereal fraction, we obtained 32 g non-crystalline mixture of bases, from the chloroform — 12 g of dark resinous material. The total alkaloid content was 0.7% of the weight of dry plant. From the bases of the ethereal fraction, after rubbing with acetone, we obtained 5.4 g crystalline yellow powder (A). After the acetone was evaporated off, 26 g of a non-crystalline mixture of bases (B) remained.

A solution of 5.4 g bases (A) in 75 ml $CHCl_3$ was chromatographed on 100 g Al_2O_3 and washed with $CHCl_3$. Upon elution with $CHCl_3$, we isolated 2.9 g protopine from the lower colorless zone. The bases from the upper yellow zone were eluted with methanol and after evaporation of the solvent, were repeatedly chromatographed on Al_2O_3, after being dissolved in $CHCl_3$ with 2% CH_3OH. We isolated 0.7 g of protopine and 0.3 g of a yellow base, m.p. 174-176°. The tartrate of this base melted at 212° (from aqueous alcohol), a sample mixed with fumaridine tartrate melted at the same temperature. The base that was isolated from the tartrate melted at 189-190° and melted at the same temperature when mixed with fumaridine.

A solution of 26 g bases (B) in 700 ml $CHCl_3$ was chromatographed on 500 g Al_2O_3. We obtained 7 zones of different colors. Upon elution of the lower colorless zone with $CHCl_3$, we obtained 2.2 g semicrystalline mass from which we isolated 0.4 g of fumvailine in the form of coarse crystals, m.p. 180.5-181.5° (from acetone). $[\alpha]_D - 44.4°$ (c = 4.4; $CHCl_3$). The base was not phenolic in character.

Found %: C 64.99, 64.90; H 5.31, 5.29; N 3.59, 3.56; OCH_3 15.72, 15.78. $C_{20}H_{19}O_6N$. Calculated %: C 65.04; H 5.18; N 3.79; $2OCH_3$ 16.80.

Fumvailine hydrochloride, obtained in alcoholic solution, melted at 212° (from alcohol).

Found %: C 58.48, 58.55; H 5.53, 5.38; N 3.49, 3.43; Cl 8.48, 8.52. $C_{20}H_{19}O_6N \cdot HCl$. Calculated %: C 59.19; H 4.96; N 3.45; Cl 8.73.

We could not isolate specific substances from the other 6 zones.

IV. Alkaloids of Papaver hybridum

7 kg of plants was treated as described above. From the ethereal fraction, we obtained 7 g and from the chloroform, 2 g of non-crystalline bases. The alkaloid content was 0.12% of the weight of dry plant.

An alcoholic solution of the bases from the ethereal fraction was acidified with concentrated hydrobromic acid; the hydrobromide of pagibrine came down, yield 3.2 g, thin needles, m.p. 204° with decomposition (from water). $[\alpha]_D + 44.6°$ (c = 0.83; water).

Found %: C 48.25, 48.29; H 5.23, 5.42; N 5.02, 5.32; Br 28.45, 28.17. $C_{22}H_{30}O_4N_2 \cdot 2HBr$. Calculated %: C 48.19; H 5.88; N 5.10; Br 29.14.

The base, isolated from the hydrobromide by the usual method, was an amorphous light yellow substance, soluble in all ordinary solvents except petroleum ether.

Found %: M 375 (according to Rast). $C_{22}H_{30}O_4N_2$. Calculated %: M 386.

The hydroiodide of pagibrine was obtained in acetone solution in the form of prisms, m.p. 200° with decomposition (from water).

V. Alkaloids of Roemeria hybrida

1.2 kg plants was treated as previously described. From the ethereal fraction, we obtained 7 g and from the chloroform — 2.5 g non-crystalline bases. The alkaloid content was 0.8% of the weight of dry plant.

The bases from the ethereal fraction were rubbed with a small quantity of methanol; we isolated 0.5 g protopine. The bases from the mother liquors were dissolved in acetone after isolation of protopine; upon acidification with alcoholic hydrochloric acid, 2.4 g crystalline hydrochloride separated out. The base, isolated from this hydrochloride, crystallized upon being rubbed with acetone; we isolated 0.2 g of remeridine in the form of colorless needles, m.p. 228-230° (from acetone). The substance was readily soluble in chloroform, alcohol, less in acetone; with Fried's reagent it gave an intense brown-violet coloration.

Found %: C 69.97, 70.05; H 7.29, 7.25; N 7.75, 7.87; OH 3.30, 3.67; OCH_3 17.63. M 545 (according to Rast). $C_{31}H_{39}O_5N_3$. Calculated %: C 69.77; H 7.36; N 7.87; 1 OH 3.18; $3 OCH_3$ 17.44. M 534.

Remeridine hydrochloride melted at 258-260° (from water).

Found %: Cl 12.01. $C_{31}H_{39}O_5N_3 \cdot HCl$. Calculated %: Cl 11.69.

From the chloroform fraction, after rubbing with methanol, we isolated 0.15 g base in the form of colorless needles, m.p. 230°; a sample mixed with remeridine gave a sharp melting point depression.

VI. Alkaloids of Papaver pavoninum

5.4 kg of plants was treated as previously described. From the ethereal extract we obtained 2.5 g from the chloroform – 3 g of dark non-crystalline bases. The alkaloid content was 0.1% of the weight of dry plant. From the bases of the ethereal fraction, after rubbing with methanol, we isolated 0.1 g protopine. After isolation of protopine, the alkaloids from the mother liquors were dissolved in 10% H_2SO_4, the solution was alkalized with 20% NaOH and the bases were extracted with ether. After evaporation of the ether, treatment with acetone, from the residue 0.1 g of substance separated out, m.p. 157-159° (from ethyl acetate); mixing with α-allocryptopine gave no melting point depression. The acetone mother liquor was acidified with alcoholic hydrochloric acid; 0.3 g hydrochloride came down, m.p. 248-250° (from alcohol). The base, isolated from the hydrochloride (0.2 g), partially crystallized upon standing. After treatment with acetone, we isolated 0.1 g of substance, m.p. 226-228° (from alcohol); mixing with remeridine gave no melting point depression.

VII. Alkaloids of Chelidonium majus

8 kg plants was treated as the previous plants. Upon shaking a dichloroethane extract with 10% H_2SO_4, an orange precipitate of sulfates (2 g) came down. After alkalization with aqueous ammonia, from the aqueous solution we extracted 53 g of non-crystalline bases with chloroform. The alkaloid content was 0.7% weight of dry plant.

From the sulfates, difficultly soluble under the conditions described in the literature [4], we isolated: a base which melted at 240-242° (from ether), evidently sanguinarine (literature gives m.p. 242-243°)and a tartrate that melted at 210-213° (from alcohol), evidently the tartrate of chelerythrine (literature gives m.p. 214-216°).

The total bases from the chloroform extract was rubbed with a small quantity of methanol and from the undissolved residue (6 g), after three crystallizations from a mixture of alcohol and chloroform, we isolated 1 g of chelidamine – faintly yellow needles, m.p. 204-205°.

The substance, readily soluble in chloroform, poorly – in alcohol, acetone and in ether, insoluble in water and in alkalis, was unchanged by the action of diazomethane in methanol; a mixture with protopine gave a sharp melting point depression. $[\alpha]_D - 316.9°$ (c = 4.4; $CHCl_3$).

Found %: C 70.46; H 5.47, 5.43; N 4.47, 4.35. $C_{19}H_{19}O_4N$. Calculated %: C 70.14; H 5.88; N 4.30.

Chelidamine hydrochloride was obtained by acidification of the chloroform solution of the base with alcoholic hydrochloric acid; recrystallized from water, it melted at 254-256°.

Found %: C 62.61, 62.60; H 5.28, 5.02; N 4.10, 3.77; Cl 10.11. $C_{19}H_{19}O_4N \cdot HCl$. Calculated %: C 63.00; H 5.77; N 3.78; Cl 9.80.

Chelidamine methiodide was obtained by boiling a solution of the base in methanol with an excess of methyl iodide for 2 hours; it melted at 275° (from water).

The bases obtained from the mother liquors after isolation of chelidamine, were dissolved in 10% HCl; the solution was repeatedly extracted with chloroform. From the chloroform extract we obtained 20 g non-crystalline hydrochlorides which were converted to the bases; from the latter, we isolated 1 g protopine. After alkalization with 10% NaOH, extraction of the aqueous hydrochloric acid solution by chloroform yielded 25 g non-crystalline bases, which, upon treatment with acetone, yielded 2 g of protopine. The acetone mother liquor was concentrated; after addition of alcoholic hydrochloric acid to the residue, we isolated 5 g of insoluble hydrochloride, m.p. 300° (from water). The base, isolated from the hydrochloride, melted at 133° (from alcohol), $[\alpha]_D + 110°$ (c = 3.6; $CHCl_3$).

Found %: C 65.41; H 5.72; N 3.33. $C_{20}H_{19}O_5N$. Calculated %: C 64.85; H 5.44; N 3.78.

The hydrochloride prepared from the base melted at 295° (from alcohol).

Found %: C 61.90; H 5.00; N 3.51. $C_{20}H_{19}O_5N \cdot HCl$. Calculated %: C 61.62; H 5.17; N 3.59.

The properties and composition of the alkaloid isolated proved that it was chelidonine, ($C_{20}H_{19}O_5N$, m.p. 136°, $[\alpha]_D + 115°$).

SUMMARY

The alkaloidal content of 11 types of plants, belonging to the poppy family (Papaveraceae), was investigated: Fumaria Schleicheri Soy-Will., F. micrantha Lag., F. Vaillantii, Papaver hybridum L., P. pavoninum, Roemeria hybrida, Glaucium corniculatum, G. flavum, G. Squamigerum Kar. and Kir., Chelidonium majus, Hypecoum pendulum.

The following new alkaloids were isolated: fumaridine ($C_{23}H_{28}O_5N_2$), fumaramine ($C_{21}H_{22}O_5N_2$), fumaritine ($C_{20}H_{21}O_5N$), fumarinine ($C_{16}H_{15}O_4N$), fumvailine ($C_{20}H_{19}O_6N$), pagibrine ($C_{22}H_{30}O_4N_2$), remeridine ($C_{31}H_{39}O_5N_3$) and chelidamine ($C_{19}H_{19}O_4N$).

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CONJUGATED ADDITION REACTIONS OF HALOGENS TO OLEFINS

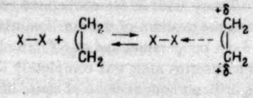
V. NITROGEN β-HALOALKYLATION

A. I. Titov and V. G. Kuzmin

The studied reactions of halogens (X_2) with olefins were called conjugated for the reason that they draw a third component into reaction, for example A–H, in itself not reacting with the multiple (double) bond:

$$X_2 + \overset{-\delta}{C}H_2 = \overset{-\delta}{C}H_2 + A{-}H \longrightarrow X{-}CH_2{-}CH_2{-}A + HX. \quad (1)$$

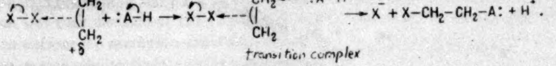
In our opinion, first developed in 1943-1946 [1], these conjugated reactions begin with the formation of Complex (2) as the result of the π-electrons of the olefin, shown in the scheme by a small bow, entering into the sphere of the electrophilic halogen [2]:



$$X{-}X + \left(\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}\right. \rightleftarrows X{-}X \leftarrow\text{---} \left(\begin{matrix} \overset{+\delta}{C}H_2 \\ \| \\ \underset{+\delta}{C}H_2 \end{matrix}\right. . \quad (2)$$

In part, our postulations have some general features in common with the hypothesis of Dewar on the mechanism of bromine cation addition to ethylene [3].

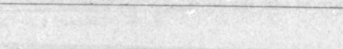
Due to the high electrophilic properties possessed by the carbons (+ δ) and their spatial accessibility, and also because of the possibility of augmenting the indicated electron shifts during chemical reaction, the Complex (2) is a vigorous β-haloalkylation agent, for example, for the A^- anions or the : A–H molecules, which leads to the realization of the conjugated reaction:



$$\overset{\frown}{X}{-}X \leftarrow\text{---} \left(\begin{matrix} \overset{+\delta}{C}H_2 \\ \| \\ \underset{+\delta}{C}H_2 \end{matrix}\right. + :\overset{\frown}{A}{-}H \longrightarrow \overset{\frown}{X}{-}X \leftarrow\text{---} \left(\begin{matrix} CH_2 \leftarrow\text{---} :\overset{\frown}{A}{-}H \\ \| \\ CH_2 \end{matrix}\right. \longrightarrow X^- + X{-}CH_2{-}CH_2{-}A: + H^+ . \quad (3)$$

transition complex

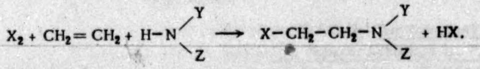
In previous communications [4-6] we described various examples of β-haloalkylation on the halogen and oxygen atoms of suitable compounds. These reactions proceeded with special success in the cases where strong acids were used as the third component A–H. The reactions for oxygen β-haloalkylation were always accompanied by the greater or less formation of the dihalo compounds $X{-}CH_2{-}CH_2{-}X$, since the hydrogen halide H–X arising in Equation (1), and especially the halogen anion, also easily react with the complex (to distinguish between the two the halogen from the anion is underlined):



$$\overset{\frown}{X}{-}X \leftarrow \left(\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}\right. + \underline{X}^- \longrightarrow X^- + X{-}CH_2{-}CH_2{-}\underline{X} \quad (4)$$

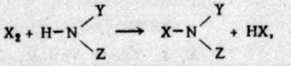
This circumstance was the chief obstacle to the successful realization of the desired conjugated reaction.

In the present study we realized the β-haloalkylation of nitrogen by the conjugated reaction method:

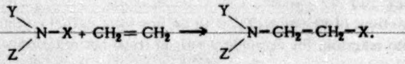


$$X_2 + CH_2{=}CH_2 + H{-}N\begin{matrix}Y\\Z\end{matrix} \longrightarrow X{-}CH_2{-}CH_2{-}N\begin{matrix}Y\\Z\end{matrix} + HX. \qquad (5)$$

We failed to find any information in the literature on the possibility of realizing such reaction. Of some interest were the studies on the reaction of N-haloamines and haloamides with olefins, since at the start of our work we did not exclude the possibility of the conjugated reaction proceeding through the intermediate formation of the N-halo derivatives:



$$X_2 + H{-}N\begin{matrix}Y\\Z\end{matrix} \longrightarrow X{-}N\begin{matrix}Y\\Z\end{matrix} + HX, \qquad (6)$$



$$\begin{matrix}Y\\Z\end{matrix}N{-}X + CH_2{=}CH_2 \longrightarrow \begin{matrix}Y\\Z\end{matrix}N{-}CH_2{-}CH_2{-}X. \qquad (7)$$

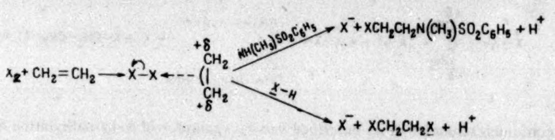
At any rate, from previous data [7-10] and from our experiments with N-dichlorobenzenesulfonamide and N-bromomethylbenzenesulfonamide, it follows that for all practical purposes ethylene fails to enter into this type of reaction.

In our first experiments of running the (5) type of conjugated reactions we used disulfonimides [11] of the $ArSO_2{-}NH{-}SO_2Ar'$ type as the third component, possessing a well-defined acid character, which permitted us to hope that they would behave just like ordinary acids in the conjugated reactions. However, the experiments on the reaction of ethylene with halogens in the medium of the disulfonimide p-$CH_3C_6H_4SO_2NHSO_2C_6H_5$ at 120° and in o-$CH_3C_6H_4SO_2NHSO_2C_6H_5$ at room temperature and at 60° failed to justify this hope – the $XCH_2CH_2N(SO_2Ar)_2$ was not formed, and the reaction mass was completely soluble in dilute soda solution. It is possible that chemical reaction was made difficult here because of steric hindrance.

The experiments on the reaction of ethylene with bromine and chlorine in N-methylbenzenesulfonamide medium led to a partial realization of the desired conjugated reaction:

$$Br_2 + CH_2{=}CH_2 + HN(CH_3)SO_2C_6H_5 \longrightarrow BrCH_2CH_2N(CH_3)SO_2C_6H_5 + HBr, \qquad (8)$$

but in the main the reaction proceeded with the formation of the dihaloethane in accord with the (4) type of reaction. As a result, of the two reactions possible for the complex that of


X₂ + CH₂=CH₂ ⟶ X–X ← - - - (CH₂ ∥ CH₂)
+δ
+δ
HN(CH₃)SO₂C₆H₅
X⁻ + XCH₂CH₂N(CH₃)SO₂C₆H₅ + H⁺
X–H
X⁻ + XCH₂CH₂X + H⁺

(9)

(10)

direction (10) predominated – the activity of the sulfonamide proved to be considerably less than that of the hydrogen halide or, more probably, its solvate.

The structure of the β-chloroethylmethylbenzenesulfonamide $ClCH_2CH_2N(CH_3)SO_2C_6H_5$ and β-bromoethylmethylbenzenesulfonamide $BrCH_2CH_2N(CH_3)SO_2C_6H_5$, obtained by the conjugated reaction method, was proved by establishing the identity of these products with the compounds that we had synthesized by the alkylation of potassium methylbenzenesulfonamide with either the corresponding β-haloethyl sulfates or aryl sulfonates, for example, in accord with the equation:

$$p\text{-}\mathrm{CH_3C_6H_4SO_3CH_2CH_2Br + KN(CH_3)SO_2C_6H_5} \longrightarrow$$

$$\longrightarrow \mathrm{BrCH_2CH_2N(CH_3)SO_2C_6H_5} + p\text{-}\mathrm{CH_3C_6H_4SO_3K}. \qquad (11)$$

If the absence of the reaction between $C_6H_5SO_2N(CH_3)Br$ and $C_6H_5SO_2N(CH_3)Cl$ with ethylene is taken into consideration, then our syntheses of β-haloethylsulfonamides by the reaction of halogens with an olefin in the sulfonamide medium is direct proof that the conjugated addition processes proceed, not through the intermediate reaction of the halogens with the third component by the (6) and (7) equation types, but actually, by the conjugation reaction mechanism in the narrow sense of the word, for example, by Equation (9).

EXPERIMENTAL

1. Alkylation of potassium methylbenzenesulfonamide with β-haloethyl esters of strong acids. a) Preparation of β-chloroethylmethylbenzenesulfonamide. A mixture of 11.0 g potassium methylbenzenesulfonamide and 11.8 g dichlorodiethyl sulfate was heated for 4 hours at 65°. The product was mixed with 20 ml water and 30 ml ether and the organic layer was then treated with 10 ml 5% caustic potash. After drying with sulfate and evaporation of the ether, 9.1 g of oil remained in the flask which crystallized upon being rubbed with a small rod. After crystallization from alcohol, we isolated 4.6 g pure β-chloroethylmethylbenzenesulfonamide which melted as per literature data at 65° [12]. Alkylation with β-chloroethylbenzenesulfonate gave a slightly smaller yield of product.

Found %: Cl 15.35. $C_9H_{12}O_2NSCl$. Calculated %: Cl 15.17.

The product was prepared previously by Marckwald and Frobenius by the action of N-methylethyleneimine on benzenesulfochloride [12].

$$\mathrm{\overset{\curvearrowleft}{Br{-}H} \longleftarrow NH(CH_3)SO_2C_6H_5.}$$

In our experiments β-chloroethylmethylbenzenesulfonamide readily distilled in vacuum; b.p. 178° at 7 mm and 167° at 3 mm. The boiling point of unsubstituted methylbenzenesulfonamide (189° at 7 mm) was slightly higher, due apparently, to the presence of hydrogen bonds.

b) Preparation of β-bromoethylmethylbenzenesulfonamide. A mixture of 4.2 g potassium methylbenzenesulfonamide and 5.6 g of β-bromoethyl-p-toluenesulfonate was heated and treated as described above. After evaporation of ether, 5.4 g oil remained. The fraction of this oil which boiled at 170-180° solidified upon cooling. Upon recrystallization from alcohol, small colorless prisms, m.p. 76°, separated out. Analysis of the product and its properties showed it to be the previously unknown β-bromoethylmethylbenzenesulfonamide.

Found %: Br 28.49, 28.56. $C_9H_{12}O_2NSBr$. Calculated %: Br 28.73.

2. β-Haloalkylation of methylbenzenesulfonamide by the method of coupling reactions. a) Preparation of β-chloroethylmethylbenzenesulfonamide. A fusion of 100 g of distilled methylbenzenesulfonamide, with mechanical stirring, was saturated in a glass reactor [2, 4] in the course of 20 hours with chlorine and ethylene (a slight excess of the latter) until 50 g weight addition. Dichloroethane (42 g) was driven off from the reaction product and the residue was then distilled at 197-200° (11 mm). This fraction was treated with 250 ml of 4 % caustic soda solution to extract the methylbenzenesulfonamide from it. The insoluble crystalline precipitate, m.p. 60-61°, was quite pure β-chloroethylmethylbenzenesulfonamide. After crystallization from alcohol, it melted at 64° and gave no melting point depression when mixed with the product obtained by alkylation with dichlorodiethyl sulfate. Its yield was 11 g (about 10% based on the sum of reaction products).

b) 90 g of bromine was poured in separate portions into a fusion of 70 g of N-methylbenzenesulfonamide with mechanical stirring and the reaction mixture was then saturated with 15 liters of ethylene. 90 g of dibromoethane was then driven off from the reaction mixture at 48° (23 mm). The residue was treated in several stages with 250 ml of 4% caustic soda solution. The insoluble crystalline β-bromoethylmethylbenzenesulfonamide, m.p. 74°, weighed 9.2 g. After crystallization from alcohol, the product melted at 76-77° and gave no melting point depression in a sample mixed with β-bromoethylmethylbenzenesulfonamide prepared by the alkylation of potassium methylbenzenesulfonamide with β-bromoethyl-p-toluenesulfonate.

3. Reaction of ethylene with N-halomethylbenzenesulfonamides. 50 g of N-chloromethylbenzenesulfonamide was saturated with ethylene at 60° in a reactor with mechanical stirring. After all the air had been

removed and the apparatus was hermetically sealed, no signs of ethylene absorption were apparent. The same results were obtained in an experiment with a mixture of N-bromomethylbenzenesulfonamide and dichloroethane.

SUMMARY

1. The β-haloalkylation of nitrogen was accomplished by the method of conjugated reactions: the reaction of halogens with ethylene in N-methylbenzenesulfonamide medium gave β-chloroethylmethylbenzenesulfonamide and β-bromoethylmethylbenzenesulfonamide.

2. It was found that the N-bromo and N-chloromethylbenzenesulfonamides fail to react with ethylene, and thus it was directly shown that the conjugation reaction, proceeding in accord with Equation (1) through the intermediate formation of N-haloamides, is absent.

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THE MECHANISM OF INHIBITOR ACTION

L. I. Kashtanov and N. V. Kazanskaya

We had established that the same inhibitors can exert a hindering action on the oxidation of extremely different substances. In addition, the oxidation of the same substance can be inhibited by different inhibitors [1].

Below, in Table 1, we present some additional material to that published earlier and the action of different inhibitors is compared (our new data are marked with an asterisk).

From the data in Table 1 it can be seen that a close interrelationship exists between the inhibitors and the inhibited substance. It is even possible to make the definite postulation that the same inhibitor can inhibit any oxidative process.

All of our presented inhibitors show polarity, and the dipole moment of the inhibitor possesses great significance in hindering oxidation reactions [3, 4, 5]. It was shown that hydroquinone, p-aminophenol, glycerol, p-phenylenediamine and pyrocatechol, being inhibitors for the oxidation of sodium sulfite, are in turn themselves inhibited by sodium sulfite [14]. Attention is drawn to the fact that phenol [25] and hydroquinone [14] are stabilizers for sodium sulfite and for sulfur dioxide, while sodium sulfite is in turn a stabilizer for phenol [7] and hydroquinone [14]. It was established that phenol and hydroquinone give compounds of the solvated type with sulfur dioxide [12, 16]. These data were again confirmed by us when we studied the mechanism of the inhibiting action shown by aromatic amines [4]; in this study we isolated some unstable compounds between the inhibitor and inhibited substance. In addition, we isolated the solvated type of compound for pyrogallol and pyrocatechol with sulfur dioxide [16].

Wieland and Franke [7], who explained the hindering action exerted by sodium sulfate on the oxidation of ferrous chloride as being due to the formation of a complex salt, also arrived at similar conclusions. Having studied the action of inhibitors, S. A. Balezin [13], and N. F. Ermolenko and E. N. Novikova [5] also adhere to the same viewpoint.

As a result, the mechanism of inhibitor action consists in the formation of unstable compounds between the inhibitor and substance being inhibited.

We ran some experiments on the oxidation of sodium sulfite in the presence of hydrochloric acid, urotropine (hexamethylenetetramine) and peroxide-free diethyl ether. The apparatus used for the experiments and the experimental conditions were described earlier [1]. The inhibitors were used in concentration of 0.05 and 0.1%. The experimental data are given below in Table 2.

As can be seen from the data given in Table 2, hydrochloric acid functions as an inhibitor; its retarding action on the oxidation of sodium sulfite is stronger than that of urotropine. Diethyl ether shows the greatest retarding action on the oxidation of sodium sulfite. As a result, our experimental data revealed that diethyl ether is not only an inhibitor for the oxidation of benzaldehyde and stannous chloride, but also for sodium sulfite. Hydrochloric acid inhibits the oxidation of not only hydrogen sulfide and ferrous chloride, but also of sodium sulfite. In turn urotropine inhibits the oxidation of hydrogen sulfide and sodium sulfite. Our experimental data show good agreement with the data of S. A. Balezin and S. S. Gerasimov [8], who also found that hydrochloric acid is a stronger inhibitor for the oxidation of hydrogen sulfide than is urotropine.

TABLE 1

Expt. Nos.	Inhibitor	Inhibited substance
1	Sulfur dioxide and sodium sulfite	Phenol [7], hydroquinone [14, 2], p-aminophenol [14], glycerol [14, 17], p-phenylenediamine [14], pyrocatechol [14], benzaldehyde [18], $FeCl_2$ [7].
2	Hydroquinone	Gasoline [15], isopropyl ether [24], fish and sea-life oils [26], benzaldehyde [7], H_3PO_2 [7], Na_2SO_3 [14], H_3AsO_3 [7], olefins [7], isostilbene [7], acetaldehyde [7].
3	Aniline	Rubber [27], $Sn^{\cdot\cdot}$ [7], $Fe^{\cdot\cdot}$ [7], benzaldehyde [22], Na_2SO_3 [1]
4	m-Toluidine	Na_2SO_3 [1]
5	o-Toluidine	Na_2SO_3 [1]
6	p-Toluidine	Na_2SO_3 [1]
7	Stannous tin	$Fe^{\cdot\cdot}$ [19], Na_2SO_3 [23]
8	Camphor	Na_2SO_3 [7], H_2S [11]
9	Glycerol	H_2S [6], Na_2SO_3 [18]
10	Phenol	Na_2SO_3 [25], $SnCl_4$ [10], chloroform [7], rubber [7]
11	Urotropine	H_2S [8], Na_2SO_3 *
12	Diethyl ether	Na_2SO_3 *, $SnCl_2$ [9], benzaldehyde [7]
13	Pyrogallol	Olefins [20], hexaphenylethane [7], unsaturated oils and vitamins [7], dipentene [5], triphenylmethyl [21]
14	α-Naphthol	H_2S [7], gasoline [15]
15	Aminophenol	$FeCl_2$ [22], Na_2SO_3 [22]
16	β-Naphthol	Dipentene [5]
17	α-Naphthylamine aldol	Rubber [1], Na_2SO_3 [1]
18	Phenyl-β-naphthylamine	Rubber [1], Na_2SO_3 [1]
19	α-Naphthylamine	Olefins [20], organic monomers [20]
20	β-Napthylamine	Olefins [20], organic monomers [20]
21	Hydrochloric acid	H_2S [8], Na_2SO_3 *, $FeCl_2$ [7]
22	Formaldehyde	H_2S [8], benzaldehyde [7], Na_2SO_3 [13]

TABLE 2

Inhibitor	Degree of Na_2SO_3 oxidation (in %) with time (in minutes)					
	5	15	25	35	45	55
0.05% Urotropine solution	13.7	27.2	36.2	50.9	58.1	65.4
0.1% Urotropine solution	13.0	23.4	35.6	42.6	44.3	47.9
0.16% Hydrochloric acid solution	4.4	5.3	5.3	7.1	8.3	10.7
Diethyl ether	2.8	2.8	2.8	2.8	2.8	2.8
Without inhibitor	13.9	41.3	69.0	94.8	98.2	100

SUMMARY

1. The constancy of the mechanism of inhibitor action in the retardation of oxidative reactions was established.

2. The inhibitor forms a solvate-type of compound with the substance being inhibited, which serves as the reason for the hindering effect.

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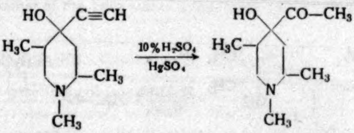
ACETYLENE DERIVATIVES

171. HETEROCYCLIC COMPOUNDS. XXXII. HYDRATION OF HETEROCYCLIC ALCOHOLS AND GLYCOLS OF THE ACETYLENE SERIES

I. N. Nazarov and L. N. Ivanova

The hydration of heterocyclic acetylene and vinylacetylene alcohols has remained completely unstudied up to now. It appeared of interest to realize such hydration as being a method capable of leading to the synthesis of compounds, deserving attention for their physiological activity.

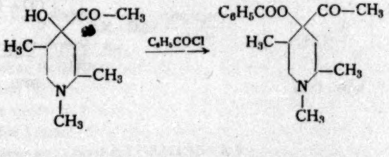
The hydration of the low-melting and high-melting isomers of 1,2,5-trimethyl-4-ethynyl-4-piperidol (m.p. 110-111° and 177-178° [1]) in dilute sulfuric acid, in the presence of mercuric sulfate, leads to the formation of the α- and β-isomers of 1,2,5-trimethyl-4-acetyl-4-piperidol with m.p. 129-130° and 59-60°, respectively.



α-isomer (I), m.p. 110-111°;
β-isomer (II), m.p. 177-178°;

α-isomer (III), m.p. 129-130°;
β-isomer (IV), m.p. 59-60°.

The reaction of the 1,2,5-trimethyl-4-acetyl-4-piperidol α-isomer (III) with benzoyl chloride gave the benzoate α-isomer (V) with b.p. 187-188° at 2 mm. Under similar conditions the 1,2,5-trimethyl-4-acetyl-4-piperidol β-isomer (IV) gave the benzoate β-isomer (VI) with m.p. 100-101°.

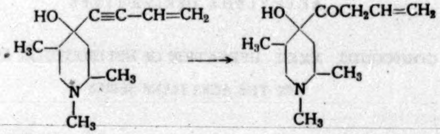


α-isomer (III), m.p. 129-130°;
β-isomer (IV), m.p. 59-60°.

α-isomer (V), liquid;
β-isomer (VI), m.p. 100-101°.

The stable crystalline hydrochlorides of both benzoate isomers of 1,2,5-trimethyl-4-acetyl-4-piperidol (m.p. 170-171° and 155-156°) were tested pharmacologically. The testing revealed that these compounds possess fairly strong anesthetic activity and exceed that of novocaine by approximately 2-2.5 times. The benzoate α-isomer is the more active of the two. However, both of these compounds show fairly strong irritant action.

We also studied the hydration of the two isomers (VII) and (VIII) of 1,2,5-trimethyl-4-vinylethynyl-4-piperidol with m.p. 82-83° and 112-112.5°, respectively. The isomer of this alcohol with m.p. 112-112.5° was previously unknown; it is the third isomer in addition to the first two with m.p. 82-83° and 96-97°, obtained earlier in our laboratory [1].

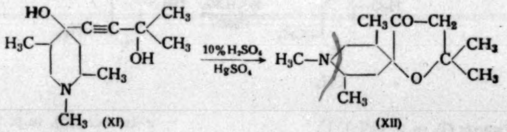


α-isomer (VII); m.p. 82-83°;
γ-isomer (VIII), m.p. 112-112.5°.

α-isomer (IX), liquid;
γ-isomer (X), liquid.

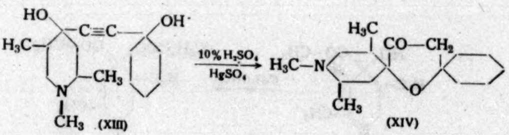
The hydrogenation of the double bond and the esterification of the hydroxyl group present in the two isomeric keto alcohols (IX) and (X) obtained in this manner can lead to a series of compounds with physiological activity.

We also realized the hydration of the two heterocyclic acetylene γ-glycols (XI) and (XIII), containing the piperidine ring and described in the previous communication [2]. Similar to the aliphatic and alicyclic acetylene γ-glycols [3], this hydration proceeds with the formation of tetrahydrofuranones, i.e. together with hydration of the triple bond there occurs the cleavage of water at the expense of the hydroxyl groups. The heating of the acetylene glycol (XI) with 10% sulfuric acid in the presence of mercuric sulfate gave the tetrahydrofuranone (XII) in about 50% yield:



(XI) (XII)

The hydration of the acetylene glycol (XIII) under similar conditions leads to the formation of the tetrahydrofuranone (XIV) with two spiran rings:



(XIII) (XIV)

EXPERIMENTAL

α-Isomer of 1,2,5-trimethyl-4-acetyl-4-piperidol (IV). 4 g mercury sulfate, 80 ml water and 8 ml sulfuric acid (d_4^{20} 1.83) were placed in a flask fitted with stirrer and reflux condenser. Upon stirring, 9.6 g of the low-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (I) (m.p. 110-111°) in 80 ml of water was added to the reaction mixture. The latter was heated on a boiling bath for 8 hours. The next day the solution was filtered, concentrated in vacuum, the residue was saturated with potash and the supernatant oil was extracted with ether. The ethereal extract was dried with potash, the ether was driven off, and the residue crystallized. We isolated 6.2 g 1,2,5-trimethyl-4-acetyl-4-piperidol (III), m.p. 129-130° (from petroleum ether). The yield was 58% based on the acetylenic alcohol taken.

Found %: C 65.32, 65.43; H 10.56, 10.60; N 7.56, 7.72. $C_{10}H_{19}O_2N$. Calculated %: C 65.00; H 10.25; N 7.60.

β-Isomer of 1,2,5-trimethyl-4-acetyl-4-piperidol (III). 2 g mercury sulfate, 20 ml water and 2 ml sulfuric acid (d_4^{20} 1.83) were placed in a flask. Upon stirring, 2.2 g of the high-melting isomer of 1,2,5-trimethyl-4-ethynyl-4-piperidol (II) (m.p. 177-178°) in 20 ml of water, was added to the reaction mixture. The latter was heated over a boiling bath for 6 hours. The product was treated as described above. After the ether was driven off, the residue crystallized. We isolated 1.7 g 1,2,5-trimethyl-4-acetyl-4-piperidol (IV), m.p. 59-60° (from petroleum ether, boiling range 40-60°). The yield was 70% based on the acetylenic alcohol taken.

Found %: C 65.70, 65.60; H 10.31, 10.48; N 7.80, 7.54. $C_{10}H_{19}O_2N$. Calculated %: C 65.00; H 10.25; N 7.60.

Benzoate of 1,2,5-trimethyl-4-acetyl-4-piperidol (α-isomer) (V). A mixture of 3 g 1,2,5-trimethyl-4-acetyl-4-piperidol (III) (m.p. 129-130°) and 7 ml benzoyl chloride was heated for 20 minutes at 140-145°, after which we added 7 ml more benzoyl chloride and the heating was continued for 30 minutes at 160-165°. The benzoyl chloride was driven off in vacuum, 4 ml of water was added and the neutral products were extracted from the acidic solution with ether. The aqueous layer was treated with potash and the supernatant oil was repeatedly extracted with ether. The ethereal extract was dried with sodium sulfate, the ether was driven off and the product was distilled in vacuum. We isolated 3 g of the α-isomer of the benzoate of 1,2,5-trimethyl-4-acetyl-4-piperidol (V), b.p. 187-188° at 2 mm. The yield was 64% based on the keto alcohol taken for the reaction.

Found %: C 70.75, 70.92; H 8.09, 8.08; N 4.84, 4.73. $C_{17}H_{23}O_3N$. Calculated %: C 70.55; H 8.01; N 4.85.

The hydrochloride of the α-isomer of the benzoate of 1,2,5-trimethyl-4-acetyl-4-piperidol (V) melted at 170-171° (from alcohol).

Found %: Cl 10.52, 10.64. $C_{17}H_{24}O_3NCl$. Calculated %: Cl 10.88.

Benzoate of 1,2,5-trimethyl-4-piperidol (β-isomer) (VI). 0.5 g 1,2,5-trimethyl-4-acetyl-4-piperidol (IV) (m.p. 59-60°) and 2.5 ml benzoyl chloride were heated 20 minutes at 140-145°. 2.5 ml more benzoyl chloride was then added and heating was continued for 30 minutes at 160-165°. Further treatment was as described above.

After the ether was driven off, the residue (0.6 g) crystallized. We isolated 0.35 g of the β-isomer of the benzoate of 1,2,5-trimethyl-4-acetyl-4-piperidol (VI), m.p. 100-101° (from petroleum ether with boiling range 40-60°). The yield was 44.8%, based on the keto alcohol taken for the reaction.

Found %: N 4.87, 4.68. $C_{17}H_{23}O_3N$. Calculated %: N 4.85.

The hydrochloride of the β-isomer of the benzoate of 1,2,5-trimethyl-4-acetyl-4-piperidol (VI) melted at 155-156°.

Found %: Cl 10.80, 10.73. $C_{17}H_{24}O_3NCl$. Calculated %: Cl 10.88.

1,2,5-Trimethyl-4-vinylethynyl-4-piperidol. 41.5 g powdered caustic potash and 415 ml dry ether were placed in a round-bottomed 3-necked flask fitted with stirrer, mercury seal, thermometer and dropping funnel. 61.7 g 1,2,5-trimethyl-4-piperidone [4] (b.p. 84° at 14 mm, n_D^{20} 1.4590) and 41.5 g vinylacetylene in 170 ml dry ether were added at −5° in the course of 2 hours to the reaction mixture with intense stirring. Stirring with ice-water cooling was continued for 5 hours. The next day 42 ml water was added at −5°, with stirring, to the reaction mixture. The ethereal layer was separated, the aqueous layer was saturated with solid caustic potash and repeatedly extracted with ether. The ethereal extract was neutralized with carbonic acid and dried with sodium sulfate. After the ether was driven off, the residue crystallized. Fractional crystallization from gasoline (boiling range 80-100°) yielded 33.7 g of the β-isomer, m.p. 96-97°, 16.4 g of the low-melting α-isomer (VII), m.p. 82-83° and 2.5 g of the high-melting γ-isomer (VIII), m.p. 112-112.5°. Besides this, we obtained 24.3 g of an unresolved mixture of isomers. The total yield, based on the piperidone taken, was 91%. The isomer that melted at 112-112.5° was isolated first.

Found %: N 7.08, 6.98. $C_{12}H_{19}ON$. Calculated %: N 7.29.

1,2,5-Trimethyl-4-vinylacetyl-4-piperidol (IX). 9.7 g 1,2,5-trimethyl-4-vinylethynyl-4-piperidol, m.p. 82-83° (VII), 100 ml 10% sulfuric acid and 2 g of mercury sulfate were placed in a flask. The reaction mixture was heated on a boiling water bath for 10 hours. The solution was filtered, concentrated in vacuum and the residue was saturated with potash, extracted with ether and dried with sodium sulfate. After the ether was driven off, the product was distilled in vacuum. We isolated 4.7 g of substance, b.p. 110-120° at 5 mm. After a repeated distillation, we isolated 2.3 g 1,2,5-trimethyl-4-vinylacetyl-4-piperidol (IX), b.p. 105-107° at 3 mm. The yield of pure product was 22%.

Found %: N 6.46, 6.45. $C_{12}H_{21}O_2N$. Calculated %: N 6.63.

The methiodide of 1,2,5-trimethyl-4-vinylacetyl-4-piperidol (IX) melted at 233-235° (from alcohol). The 2,4-dinitrophenylhydrazone of the methiodide melted at 339° (with decomp.).

Found %: N 12.70, 13.00. $C_{19}H_{28}O_5N_5I$. Calculated %: N 13.13.

1,2,5-Trimethyl-4-vinylacetyl-4-piperidol (X). We took 2.25 g 1,2,5-trimethyl-4-vinylethynyl-4-piperidol (VIII) (m.p. 112-112.5°), 50 ml 10% sulfuric acid and 1 g mercury sulfate. The reaction mixture was heated on a boiling water bath for 3 hours. The treatment was continued as described above. We isolated 1.5 g 1,2,5-trimethyl-4-vinylacetyl-4-piperidol (X), b.p. 115° at 3 mm. After a second distillation, we isolated 0.9 g keto alcohol (X), b.p. 105-107° at 3 mm. The yield of pure product was 37%.

Found %: N 6.62, 6.48. $C_{12}H_{21}O_2N$. Calculated %: N 6.63.

The methiodide of 1,2,5-trimethyl-4-vinylacetyl-4-piperidol (X) melted at 250-252° (from alcohol).

2,2,6,8,9-Pentamethyl-1-oxa-8-azaspiro-(4,5)-decan-4-one (XII). 1 g mercury sulfate was added to a solution of 2.3 g of acetylenic glycol (XI) (b.p. 148-149° at 2 mm) in 30 ml 10% sulfuric acid in a flask fitted with stirrer and reflux condenser. Heating on a boiling water bath was continued for 6 hours. The solution was filtered, concentrated in vacuum, the residue was saturated with potash and the supernatant oil was extracted repeatedly with ether. The extract was dried with calcined potash, the ether was driven off and the product was vacuum-distilled. We isolated 1.42 g spiranic tetrahydrofuranone (XII), b.p. 108-110° at 2.5 mm; yield 62%.

d_4^{20} 0.9969, n_D^{20} 1.4774, MR_D 63.81; calc. 63.43.

Found %: C 69.03, 69.24; H 10.40, 10.36; N 6.49, 6.47. $C_{13}H_{23}O_2N$. Calculated %: C 69.29; H 10.29; N 6.22.

The methiodide of this tetrahydrofuranone (XII) melted at 286-287°; the 2,4-dinitrophenylhydrazone of the hydrochloride of the tetrahydrofuranone melted at 278-280°.

Found %: N 15.90, 16.13. $C_{19}H_{28}O_5N_5Cl$. Calculated %: N 15.86.

Spiro-2-cyclohexyl-6,8,9-trimethyl-1-oxa-8-azaspiro-(4,5)-decan-4-one (XIV). We took 13.3 g acetylenic glycol (XIII) (b.p. 170-171° at 1 mm) dissolved in 100 ml of 10% sulfuric acid and 2 g of mercury sulfate. The reaction mixture was heated on a boiling water bath for 4 hours. The treatment was performed as described above. We isolated 7.2 g tetrahydrofuranone (XIV), b.p. 152-153° at 2 mm (after a second distillation); yield 54%.

Found %: N 5.36. $C_{16}H_{27}O_2N$. Calculated %: N 5.27.

The methiodide of the tetrahydrofuranone melted at 251-253° (from alcohol).

Found %: N 3.40, 3.34. $C_{17}H_{30}O_2NI$. Calculated %: N 3.44.

The 2,4-dinitrophenylhydrazone of the methiodide melted at 218-220°.

Found %: N 11.94, 11.99. $C_{23}H_{34}O_5N_5I$. Calculated %: N 11.92.

SUMMARY

1. We were the first to study the hydration of the stereoisomeric acetylene and vinylacetylene alcohols of the piperidine series, and here we obtained the corresponding keto alcohols.

2. Esterification of the α- and β-isomers of 1,2,5-trimethyl-4-acetyl-4-piperidol gave the corresponding benzoates, which were tested for physiological activity.

3. We accomplished the hydration of the unsymmetrical heterocyclic acetylene γ-glycols into the corresponding heterocyclic tetrahydrofuranones with a spiran structure.

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* T. p. = C. B. Translation pagination.

[illegible]

7. We were the first to study the [illegible] of [illegible] of the piperidine series, and here we obtained the corresponding [illegible]

8. Identification of the α- and β-isomers of [illegible] [illegible] tested for pharmacological activity.

9. We accomplished the synthesis of the [illegible] regarding [illegible] with a [illegible] reaction.

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CYCLOALKYLATION OF AROMATIC COMPOUNDS

IX. THE REACTION OF 1-PHENYLCYCLOHEXANOL WITH BENZENE

N. G. Sidorova, N. M. Feiershtein and E. A. Kochetkova

Isomerization in the direction of approaching the phenyl and alkyl groups is usually observed in the condensations of the alkylcyclohexenes and alkylcyclohexanols with aromatic compounds in the presence of acid catalysts [1-4]. However, the isomerization does not always go to completion and the condensation products of the optically active alcohols with aromatic hydrocarbons [5] and phenols [6] in the presence of aluminum chloride show considerable optical activity. Recently it was shown by one of us [7] that the direction of this reaction depends on the reaction conditions employed and that under mild conditions it becomes possible to obtain considerable amounts of the product with unisomerized radical.

It appeared of interest to elucidate the influence of the phenyl group in similar reactions. With this in mind we studied the reaction between 1-phenylcyclohexanol and benzene in the presence of aluminum chloride.

In the alkylation of benzene with aralkyl (aliphato-aromatic) alcohols and halides the reaction proceeds without isomerization, while in the case of phenylated unsaturated compounds it proceeds the same as if an alkyl group were present in the same position. Thus, for example, styrene [8, 9], *a*-phenylethyl alcohol [10] and *a*-chloroethylbenzene [11] all give 1,1-diphenylethane when condensed with benzene, while β-phenylethyl alcohol [12] and β-chloroethylbenzene [8] give dibenzyl.

If the unsuccessful attempts of Bodroux [13] to effect condensation of 1-phenylcyclohexene with benzene are ignored, then no one has run such reactions with cyclic compounds. However, Kursanov [14] and later Nenitzescu and Curcaneanu [15] described the condensation of 1,2-dichloro- and 1,2-dibromocyclohexanes with benzene in the presence of aluminum chloride. These reactions gave a mixture of 1,3- and 1,4-diphenylcyclohexanes. It is possible that these same products are also obtained in the condensation of 1-phenylcyclohexanol with benzene. In addition, on the basis of our previous studies it might be expected that under mild conditions it would be possible to at least avoid partial isomerization and obtain 1,1-diphenylcyclohexane.

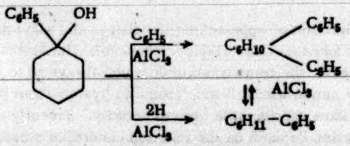
We ran the condensation of 1-phenylcyclohexanol with benzene most frequently under extremely mild conditions, hoping in this way to obtain 1,1-diphenylcyclohexane. However, in not a single instance were we able to accomplish this – the reaction products were always a mixture of the 1,3- and 1,4-diphenylcyclohexanes, phenylcyclohexane with a small amount of phenylcyclohexene as impurity, and tar.

The phenylcyclohexane obtained by us in these condensations appears as an anomalous reduction product, this type of reduction being frequently encountered when aluminum chloride is used as a catalyst [15-16]. The dimensions of the anomalous reactions in the Friedel-Crafts syntheses vary: they depend on the nature of the alkylating agent and the aromatic hydrocarbon. The reduction proceeds with especial ease in those cases where either bifunctional compounds (the intermediate reaction product is reduced) or monofunctional compounds, containing the phenyl group (the original compound is reduced), are used for the alkylation. On the other hand, from the studies of Nenitzescu and coworkers [8, 17] it can be seen that cyclohexane can be the hydrogen donor for such reactions. 1-Phenylcyclohexanol represents a combination of groups, facilitating the progress of the reduction reaction. Actually, in our case the reduction reaction was the main one – the yields ofphenylcyclohexane ranged from 29 to 66%, whereas the total yield of the diphenylcyclohexanes was only 14-22%.

To elucidate the role played by benzene in the reduction reaction we subjected 1-phenylcyclohexanol to the action of aluminum chloride in isooctane; here it was revealed that phenylcyclohexane is formed even in the absence of benzene, but in smaller amount.

Apparently, the formation of phenylcyclohexane proceeds by different paths: with benzene participation and without it. The reaction with benzene first gives diphenylcyclohexane, which under the influence of aluminum chloride is cleaved to phenylcyclohexane. By the second path it is probably not the alcohol itself that is reduced, but instead it is the chloride that is easily formed from it. Here the mixed cyclohexane hydrocarbons present in the reaction mixture are the hydrogen source, which in this connection are converted into high-molecular tarry substances.

However, it is known that phenylcyclohexane under the influence of aluminum chloride gives diphenylcyclohexanes [18], and, consequently, the diphenylcyclohexanes are also formed by two paths: in the condensation of 1-phenylcyclohexanol with benzene and in the cleavage of phenylcyclohexane. All of these reactions can be depicted by the scheme:



The reduction reaction is strongly affected by the quality of the aluminum chloride. The ease with which the reduction proceeds in the presence of hydrogen chloride [19] and water [20] additions was noted in the literature. Traces of certain salts can also strongly change the course of the reaction.

We ran a number of condensations of 1-phenylcyclohexanol with benzene in the presence of aluminum chloride with the additions of water, HCl, Cu_2Cl_2, $SnCl_4$ and $FeCl_3$, and also ran the reaction in the presence of other condensing agents: H_2SO_4, $FeCl_3$ and $AlBr_3$.

In all cases the reactions in the presence of aluminum chloride proceeded in both directions, but the yields of the phenylcylcohexane and diphenylcyclohexanes changed but slightly with change in the additions used. Traces of water and hydrogen chloride showed but slight influence; in their presence the yield of the diphenylcyclohexanes showed a slight increase, while that of the phenylcyclohexane remained nearly constant. The use of cuprous chloride and stannic chloride also proved to be of insignificant effect. The addition of ferric chloride led to obtaining only phenylcyclohexane and phenylcyclohexene. The use of pure ferric chloride for the condensation gave the same results. The use of sulfuric acid in this reaction gave a nearly theoretical yield of phenylcyclohexene.

The most interesting results were obtained with aluminum bromide. This catalyst is considered to have a similar, but more powerful action than aluminum chloride. Very little is known about its reducing properties [21]. In our case it gave the diphenylcyclohexanes in yields up to 45% and the phenylcyclohexane in 30-37% yield.

We also ran a single condensation of phenylcyclohexene with benzene in the presence of aluminum chloride. This reaction was studied by Bodroux [13], but he failed to obtain any definite results. The reaction run by us gave about 14% of diphenylcyclohexanes and 50% of the starting phenylcyclohexene was recovered unchanged.

EXPERIMENTAL

1-Phenylcyclohexanol was prepared by the Grignard reaction [22]. B.p. 150-152° (18 mm); m.p. 61°.

1-Phenylcyclohexene was prepared by heating phenylcyclohexanol with phosphoric acid at 175° for 2 hours. B.p. 100-102°(10 mm).

Reaction of 1-phenylcyclohexanol with benzene in the presence of aluminum chloride

Finely ground aluminum chloride was added in small portions with shaking to a solution of phenylcyclohexanol in benzene. After all the aluminum chloride was added, the mixture was usually set aside at room temperature for various periods of time and then gradually brought to a weak boil. Heating was continued until evolution of hydrogen chloride ceased. The mixture was decomposed by dilute hydrochloric acid and the benzene solution was washed several times with water and dried with calcium chloride and fractionated.

The following fractions were collected upon distillation: 1st, b.p. 117-121° (21 mm) – phenylcyclohexane with an admixture of phenylcyclohexene; 2nd, b.p. 180-230° (21 mm) – a mixture of 1,3- and 1,4-diphenylcyclohexanes.

The three experiments that differed most sharply in experimental conditions are described below.

1) Taken: 8.8 g (0.05 mole) 1-phenylcyclohexanol, 6.7 g (0.05 mole) $AlCl_3$ and 200 ml (2.3 mole) of benzene. After addition of $AlCl_3$, the reaction mixture was set aside at room temperature for 4 days and then heated for 30 hours at 45-50° and only at the end of this period was it heated at the boiling point. Yield of phenylcyclohexane was 5.3 g (66%) and of diphenylcyclohexanes – 1.7 g (14.4%). The residue was resinous.

2) The initial substances were taken in the same quantities. Immediately after addition of $AlCl_3$, the mixture was heated to the boiling point in the course of 3 hours. Isolated 3 g (37%) phenylcyclohexane and 1.9 g (16%) diphenylcyclohexanes. The quantity of resin was greater than in the previous experiment.

3) Taken: 4.4 g (0.025 mole) 1-phenylcyclohexanol, 5.0 g (0.037 mole) $AlCl_3$ and 100 ml benzene. Immediately after addition of $AlCl_3$, the mixture was heated with gradual rise of temperature up to 80° in the course of 3 hours. Yield of phenylcyclohexane 1.6 g (40%), of diphenylcyclohexanes – 1.3 g (22%).

Identification of reaction products. The phenylcyclohexane fraction from all of the condensations gave a positive reaction for the double bond. To remove phenylcyclohexene, the fraction was treated with hot H_2SO_4 (d 1.76), washed with water, dried and distilled. After this purification, the phenylcyclohexane crystallized upon cooling with ice and had the following constants: b.p. 230° (728 mm), d_4^{20} 0.9466, n_D^{20} 1.5287, MR_D 52.15; calc. 51.83. Its nitro compound melted at 57°, the acetamino derivative – at 127°. These results accorded well with the literature data [14].

The second fractions from all the condensations partially crystallized upon standing (the reactions performed at a higher temperature gave the most crystals). The crystals melted at 168° (from alcohol). The literature data on 1,4-diphenylcyclohexane gives m.p. 169-170° [14, 15].

Dehydrogenation of the hydrocarbon by heating with selenium at 340-380° for 2 hours yielded p-terphenyl, m.p. 210°. A mixing test with a known sample of p-terphenyl gave no melting point depression.

The liquid portion of the fraction was 1,3-diphenylcyclohexane with an admixture of the 1,4-isomer. Its dehydrogenation under same conditions yielded a small amount of p-terphenyl, m.p. 210° and mostly m-terphenyl, m.p. 88.5°. A test mixture with a known sample of m-terphenyl also melted at 88.5°.

After the phenylcyclohexane and diphenylcyclohexanes were driven off, a brown resin remained. This resin partially distilled in vacuum but no distinct fraction was obtained. Upon being heated with selenium at 350-380°, hydrogen selenide at first quite vigorously evolved but as heating progressed, its evolution slowed. After dehydrogenation, the external appearance of the resin changed only slightly and no distinct product could be obtained from it.

Reaction of 1-phenylcyclohexanol with benzene in the presence of aluminum chloride with various substances added

With addition of hydrogen chloride. 3.35 g (0.025 mole) $AlCl_3$ and 50 ml benzene were placed in a 3-necked flask fitted with mechanical stirrer, thermometer and dropping funnel and through this mixture was passed a stream of dry hydrogen chloride until the aluminum chloride dissolved (2 hours). A solution of 4.4 g (0.025 mole) 1-phenylcyclohexanol in 30 ml benzene was added drop-wise with stirring to the dark mass obtained above and the reaction mixture was then gradually heated on a water bath for 4 hours (towards completion of heating, the temperature was raised to 85°). The isolation of products was performed as usual. We obtained phenylcyclohexane, 1.4 g (35%), b.p. 100-110° (11 mm) and a mixture of 1,3- and 1,4-diphenylcyclohexanes, 1.55 g (26%), b.p. 180-220° (11 mm).

After removal of phenylcyclohexene, the 1st fraction was nitrated; we obtained p-cyclohexylnitrobenzene, m.p. 57°.

The 2nd fraction partially crystallized. The isolated crystals of 1,4-diphenylcyclohexane melted at 167°.

With addition of water. The reaction was carried out without mechanical stirring. To a solution of 4.4 g (0.025 mole) 1-phenylcyclohexanol in 75 ml (0.85 mole) benzene we gradually added 3.35 g (0.025 mole) aluminum chloride, followed by 7 drops of water. The reaction mixture was heated for 10 hours, the temperature being gradually raised to 80°. We isolated 1.7 g (42%) of phenylcyclohexane (with an admixture of phenylcyclohexene), b.p. 115-117° (20 mm) and a mixture of diphenylcyclohexanes 1.1 g (18.5%), b.p. 190-230°(20 mm). Dehydrogenation of the 2nd fraction yielded m- and p-terphenyls (m.p. 87° and 208°). Upon long standing, a small amount of crystals of 1,4-diphenylcyclohexane, m.p. 167°, separated out from the fraction containing diphenylcyclohexanes.

With addition of cuprous chloride (40% of weight of $AlCl_3$) we obtained 42% phenylcyclohexane and 10% of a mixture of 1,3- and 1,4-diphenylcyclohexanes.

With addition of stannic chloride (30% of weight of $AlCl_3$) we obtained 37.5% of phenylcyclohexane and 17% of a mixture of diphenylcyclohexanes with a preponderance of the para-isomer.

With addition of ferric chloride. In this experiment a portion of the aluminum chloride was replaced with ferric chloride: we took 2.5 g aluminum chloride and 0.83 g ferric chloride; the other substances were taken in the same amounts as in the previous experiments. The reaction mixture was heated for 12 hours. We obtained phenylcyclohexane with an admixture of phenylcyclohexene, 1.1 g (18.5%), boiling range 117-122° (22 mm).

Reaction of 1-phenylcyclohexanol with benzene in the presence of ferric chloride

The reaction was performed the same as the reactions with aluminum chloride. We took for the reaction 8.8 g (0.05 mole)1-phenylcyclohexanol, 8.1 g (0.05 mole) ferric chloride and 75 ml (0.85 mole) benzene. The mixture was gradually heated up to 75° for 4 hours and then steam-distilled. From the distillate we isolated phenylcyclohexane, b.p. 95-100° (8 mm). The yield was 3.2 g (40%). After removal of phenylcyclohexene by treatment with sulfuric acid, the phenylcyclohexane was nitrated; we obtained p-cyclohexylnitrobenzene, m.p. 57°. Its test mixture with a known sample of p-cyclohexylnitrobenzene gave no melting point depression. After steam-distillation, a solid amorphous mass remained in the flask. Diphenylcyclohexanes were not obtained in this reaction.

Reaction of 1-phenylcyclohexanol with benzene in the presence of aluminum bromide

We took 8.8 g (0.05 mole) 1-phenylcyclohexanol, 13.5 g (0.05 mole) aluminum bromide and 100 ml (1.1 mole) benzene. After addition of aluminum bromide, the mixture was left standing overnight and then heated for 7 hours, the temperature gradually being raised to 80°. We obtained 1.4 g (17.5%) phenylcyclohexane, b.p. 102-106° (10 mm) and a mixture of 1,3- and 1,4-diphenylcyclohexanes, 4.35 g (36.9%), b.p. 170-195° (8 mm). Nitration of the 1st fraction (after washing with sulfuric acid) yielded p-cyclohexylnitrobenzene, m.p. 57°. From the 2nd fraction we isolated a large amount of 1,4-diphenylcyclohexane crystals, m.p. 167°.

Performing the reaction with 1.5 g-equiv. aluminum bromide resulted in a 30% phenylcyclohexane yield and a 45% yield of diphenylcyclohexanes.

Reaction of phenylcyclohexene with benzene

A solution of 8 g (0.05 mole) phenylcyclohexene in 10 ml (0.11 mole) of benzene was gradually added to a mixture of 3.35 g (0.025 mole) of aluminum chloride and 10 ml (0.11 mole) benzene. The mixture was set aside for a day and then heated on a water bath to 80° in the course of 4 hours. We obtained 4 g (50%) phenylcyclohexene, b.p. 130-140° (40 mm) and 1.6 g (13.6%) of a mixture of diphenylcyclohexanes, b.p. 240-260° (40 mm).

The 1st fraction completely dissolved in sulfuric acid. The 2nd fraction partially crystallized, m.p. of crystals – 168°. A test mixture with 1,4-diphenylcyclohexane also melted at 168°.

Reaction of 1-phenylcyclohexanol with aluminum chloride

3.35 g (0.025 mole) $AlCl_3$ was added gradually with stirring to a solution of 4.4 g (0.025 mole) phenylcyclohexanol in 100 ml isooctane. The reaction mixture was then heated on a water bath the temperature of which was gradually raised to 80°. Heating was continued for 11 hours. Evolution of hydrogen chloride was weak. The reaction mixture was decomposed the usual way, the hydrocarbon layer was washed with water, dried with calcium chloride and distilled. After the isooctane was driven off, the residue was fractionated in vacuum. The fraction boiling at 117-122° (22 mm) was collected and analyzed. Its yield was 25% of theoretical (1 g), calculated on phenylcyclohexane.

To remove olefins, the fraction was washed with warm sulfuric acid (d 1.76) and then nitrated. We isolated p-nitrocyclohexylbenzene, m.p. 57°. A test mixture with a known sample of p-nitrocyclohexylbenzene gave no melting point depression.

Many repititions of the reaction with certain variations of the conditions of the experiments did not increase the yield of phenylcyclohexane.

SUMMARY

1. When 1-phenylcyclohexanol is reacted with benzene in the presence of aluminum chloride the main reaction is the reduction of the 1-phenylcyclohexanol to phenylcyclohexane, and condensation with the formation of the 1,3- and 1,4-diphenylcyclohexanes proceeds only to a slight degree (14-22%).

2. The use of additives with the aluminum chloride (water, hydrogen chloride, cuprous chloride and stannic chloride) fails to show much influence on the course of the reaction.

3. Only phenylcyclohexane and phenylcyclohexene were obtained when the reaction was run in the presence of an aluminum chloride-ferric chloride mixture and in the presence of ferric chloride alone.

4. Alkylation is the main direction of the reaction when 1-phenylcyclohexanol is reacted with benzene in the presence of aluminum bromide: the yields of the diphenylcyclohexane are 30-37%.

5. Only the 1,3- and 1,4-diphenylcyclohexanes (14% yield) and tar are obtained as the reaction products when phenylcyclohenene is reacted with benzene in the presence of aluminum chloride.

6. The reaction of 1-phenylcyclohexanol with aluminum chloride leads to a mixture of products, among which the presence of phenylcyclohexane was shown.

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THE SYMMETRIZATION OF METHYLETHOXYCHLOROSILANES

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The influence of various groups and atoms in organosilicon compounds on the capacity of the latter for symmetrization has been studied but slightly. It is known that asymmetrical ethoxychlorosilanes suffer decomposition when heated to give compounds possessing a symmetrical structure. Thus, for example, ethoxytrichlorosilane is decomposed to the extent of 37% when it is heated at the boiling point for 4 hours, triethoxychlorosilane is decomposed 100%, while diethoxydichlorosilane is completely stable under these conditions [1].

As our experiments revealed, the presence of a methyl group on the silicon atom in the molecule exerts a great influence on the capacity of the chloro ethers for symmetrization; methylethoxydichlorosilane and methyldiethoxychlorosilane showed considerable stability under prolonged heating.

The heating was done in the pot of a fractionation column having an efficiency of 8 theoretical plates and packed with ceramic rings. After heating for 50 hours at 100° the reaction products were fractionated, where both the methylethoxydichlorosilane and methyldiethoxychlorosilane were for the most part recovered unchanged. However, a certain reduction of the temperature in the fractionation column permits assuming the presence of some rearrangement and in this way an evaluation of the comparative stability of the methylethoxychlorosilanes can be made.

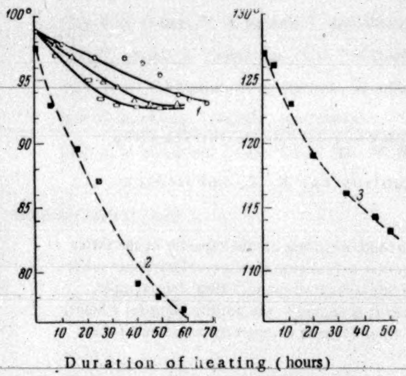
The temperature changes obtained in the fractionation column when the methylethoxydichlorosilane (Curve 1) and methyldiethoxychlorosilane (Curves 2 and 3) are heated are shown in the figure (below). The rearrangement was run at the boiling point of the products (Curves 1 and 3), and also at the same temperature of 100° (Curves 1 and 2). In the latter case the change in the boiling point of the methyldiethoxychlorosilane (when the temperature of the liquid was kept at 100°) was followed by periodically applying a slight vacuum (the residual pressure was 297 mm).

The nature of the curves shows that the methylethoxydichlorosilane apparently possesses the greater stability at the boiling point (100°), since the temperature in the fractionation column is changed but slightly after 30 to 50 hours heating, after which it becomes stabilized. For the methyldiethoxychlorosilane the decomposition, both at the boiling point (127°) and at 100°, proceeds at a considerably faster rate, since here the boiling point drops much more rapidly and fails to show a tendency to be stabilized. In the fractionation of the reaction products from the rearrangement of the methylethoxydichlorosilane the amount of the fractions, boiling below that of the starting product (93-98°), is 2%, while in the case of the methyldiethoxychlorosilane it is above 4%.

As a result, it can be assumed that a symmetrical arrangement of the chlorine atoms possesses greater significance for the thermal stability of molecules than does a symmetry of the ethoxyl groups.

EXPERIMENTAL

Preparation of methylethoxydichlorosilane and methyldiethoxychlorosilane. 897 g of methyltrichlorosilane was placed in a round-bottomed flask fitted with sealed stirrer, dropping funnel, thermometer and reflux condenser connected to a system for absorption of hydrogen chloride and then 332 g of anhydrous ethyl alcohol was introduced through the dropping funnel at 20° in the course of 4-4.5 hours. The mixture was then gradually heated up to the boiling point (99°) in the course of 2 hours after which the reaction product was cooled and separated. The yield of the mixture was 903 g (94%).



Variation of temperature in fractionating column upon heating methylethoxydichlorosilane at 100° (Curve 1) and methyldiethoxychlorosilane at 100° (Curve 2) and at 127° (Curve 3).

Fractionation of 396 g of the mixture in a column, 30 mm in diameter and 750 mm high with porcelain ring filling 4 × 1.5 × 0.5 mm, yielded a methylethoxydichlorosilane fraction, b.p. 97-99.5° (21.3%) and a methyldiethoxychlorosilane fraction, b.p. 125-127.5° (35.9%).

A second fractionation of the fraction which boiled at 97-99.5° yielded (with 31.8% yield based on initial fraction) methylethoxydichlorosilane.

B.p. 99-99.5°, d^{20} 1.068, n_D^{20} 1.380, MR_D 34.53; calc. 34.56.
Found %: SiO_2 37.7, 37.6; Cl 43.9; OC_2H_5 28.3. $C_3H_8OCl_2Si$. Calculated %: SiO_2 37.7; Cl 44.4; OC_2H_5 28.3.

Literature data [2] give: b.p. 101.2°, d^{20} 1.028.

From the fraction which boiled at 125-127.5° we isolated (yield 87.2%) methyldiethoxychlorosilane:

B.p. 126.5-127.5°, d^{20} 1.010, n_D^{20} 1.393, MR_D 40.1; calc. 40.67.
Found %: SiO_2 35.2, 35.3; Cl 20.9, 20.75; OC_2H_5 53.13. $C_5H_{13}O_2ClSi$. Calculated %: SiO_2 35.5; Cl 21.0; OC_2H_5 53.4.

Literature data [2] give: b.p. 120°, d^{20} 0.983.

Rearrangement of methylethoxydichlorosilane

144 g methylethoxydichlorosilane was placed in the still of the above described fractionating column. The temperature in the still was held at 100° for 50 hours while the reaction mixture in the column was refluxed with complete return. The temperature of the vapors in the fractionating column gradually fell to 93° (see figure, Curve 1), after which the reaction products were separated. Fractionation yielded: 1st fraction – b.p. 93-98°, 2.9 g (2.0%), %Cl 47.6; 2nd fraction – b.p. 98-99.5°, 107.8 g (74.8%), %Cl 43.9; residue above 99.5°, 27.0 g (18.9%), %Cl 37.6; losses – 6.3 g (4.3%).

The 1st fraction corresponded in chlorine content to a mixture of 89.9% methylethoxydichlorosilane and 10.9% methyltrichlorosilane which corresponded to a 0.3% methyltrichlorosilane content in the mixture obtained upon heating. In the two other experiments with methylethoxydichlorosilane, the temperature in the fractionating column also stayed at 93° (up to 75 hours of heating).

Rearrangement of methyldiethoxychlorosilane

a) At the boiling point. A similar experiment was performed with 94 g of methyldiethoxychlorosilane and after the mixture was heated for 50 hours at the boiling point (127°), the temperature in the fractionating column fell to 113° (see figure, Curve 2). Separation yielded: 1st fraction – b.p. 113-126.5°, 4.0 g (4.2%), %Cl 29.3; 2nd fraction, b.p. 126.5-127.5°, 64.5 g (68.7%), %Cl 21.6; residue above 127.5°, 23.0 g (24.5%), %Cl 17.4; losses, 2.5 g (2.6%).
The 1st fraction corresponded in chlorine content to a mixture of 35% methylethoxydichlorosilane and 65% methyldiethoxychlorosilane which corresponded to 1.5% methylethoxydichlorosilane upon calculation on the total mixture.

b) Rearrangement of methyldiethoxychlorosilane at 100°. 115 g of methyldiethoxychlorosilane was placed in the still of the above described column, a slight vacuum was connected and the still was gradually heated to 100°.

The liquid in the still was heated for 59 hours at 100°, the vacuum being periodically connected (the residual pressure was 297 mm) and the temperature was measured in the fractionating column. The liquid was then fractionated and the following fractions were obtained: 1st – b.p. 111-126.5°, 5.5 g (4.8%), %Cl 27.2; 2nd fraction – b.p. 126.5-127.5°, 71.0 g (61.6%), %Cl 21.9; residue above 127.6° – 31.0 g (27.0%), %Cl 15.7; losses – 7.5 g (6.5%).

The 1st fraction corresponded in chlorine content to a mixture of 24% methylethoxydichlorosilane and 76% methyldiethoxychlorosilane which corresponded to 1.2% methylethoxydichlorosilane upon calculation on the total mixture.

SUMMARY

1. The thermal stability of methylethoxydichlorosilane is greater than that of methyldiethoxychlorosilane, both at equal temperatures (100°) and at their respective boiling points.

2. The presence of a single methyl radical on the silicon atom in the methylethoxychlorosilane molecule sharply increases the thermal stability of the unsymmetrical compound when compared to the ethoxychlorosilanes.

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THE ACTION OF AROMATIC DIAZONIUM COMPOUNDS ON UNSATURATED COMPOUNDS

V.* AZO-COUPLING WITH SIMPLE VINYL ETHERS

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As early as 1913 K. Meyer [2] observed the reaction of p-nitrobenzenediazonium hydroxide with β-ethoxycrotonic ester, α-ethoxystyrene and ethyl vinyl ether.

The reaction was run in acetic acid solutions. Here the β-ethoxycrotonic ester was converted into the p-nitrobenzeneazoacetoacetic ester. But, as mentioned by Meyer, it is possible that the β-ethoxycrotonic ester failed to participate in this reaction, and instead it was its hydrolysis product — the aceto-acetic ester — that was involved. With respect to the structure of the substance formed from α-ethoxystyrene K. Meyer has nothing to say. In the reaction with the ethyl vinyl ether a brick-red powder was obtained. This powder could not be recrystallized. In only a single case, the conditions of which were not established exactly, did the reaction product — orange-red needles with m.p. 180° (with decomp.) — correspond by analysis to the formula $C_8H_7O_3N_3$. This permitted K. Meyer to assume that in the action of p-nitrobenzenediazonium hydroxide on the vinyl ether there occurred formation of the azo compound with the simultaneous loss of the ethoxyl group as alcohol. The structure of the reaction product was not fully established.

We set ourselves the task of first finding the optimum conditions for the azo-coupling of p-nitrobenzenediazonium hydroxide with the vinyl ether. It was revealed that the reaction proceeds smoothly in aqueous medium, under the conditions of neutralizing (to congo) the mineral acid by the addition of sodium acetate. The process was run under ice-cooling for several hours. The reaction product separated as an orange precipitate and represented a fairly pure substance. An increase in the acidity of the medium greatly lowered the yield of the azo-coupling product. In the presence of a slight excess of sodium acetate the precipitate acquired a red color. For purification the substance was treated with benzene and under heating was precipitated with water from methyl alcohol solution. Based on its analysis, chemical properties and melting point (196° with decomp.), the substance can be considered as being the mono-p-nitrophenylhydrazone of glyoxal. When treated with p-nitrophenylhydrazine it is converted into the full p-nitrophenylhydrazone of glyoxal with a melting point corresponding to that given in the literature. In the presence of hydrochloric acid the monohydrazone suffered dismutation with the formation of free glyoxal and the corresponding osazone, i.e. the di-(p-nitrophenylhydrazone) of glyoxal.

Since here the azo-coupling reaction proceeds with the cleavage of the ethoxyl group, then naturally it could be expected that in the action of the p-nitrobenzenediazonium hydroxide on other alkyl vinyl ethers the same monohydrazone of glyoxal will be formed. This was confirmed when the reaction was studied with the methyl vinyl and n-butyl vinyl ethers. The methyl vinyl ether, taken in excess, reacts rapidly with the diazo compound, giving a high yield (91%) of the hydrazone. The butyl vinyl ether, being less soluble, gives lower yields; in addition, its azo-coupling product is obtained with a red color and lends itself with difficulty to purification.

As a result, these experiments served to confirm the assumption made by K. Meyer relative to the direction of the azo-coupling reaction of vinyl ethers with aromatic diazo compounds. The substance with m.p. 180°, obtained by K. Meyer as the result of reacting p-nitrobenzenediazonium hydroxide with the ethyl vinyl ether, probably represented the impure p-nitrophenylhydrazone of glyoxal.

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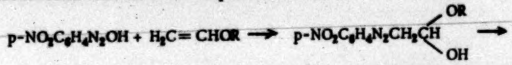
* See [1] for Communication IV.

The general reaction scheme can be depicted as follows:



$$p\text{-}NO_2C_6H_4N_2OH + H_2C{=}CHOR \longrightarrow p\text{-}NO_2C_6H_4N_2CH_2CH\genfrac{}{}{0pt}{}{OR}{OH} \longrightarrow$$

$$p\text{-}NO_2C_6H_4N{=}NCH_2CHO \longrightarrow p\text{-}NO_2C_6H_4NHN{=}CHCHO.$$

Working with the n-butyl vinyl ether it was qualitatively shown that the diazotized o- and p-nitroanilines can also enter into the azo-coupling reaction.

EXPERIMENTAL

Diazotization of p-nitroaniline. 3.5 g p-nitraniline was dissolved with heating in a mixture of 7.5 ml concentrated hydrochloric acid and 20 ml water. A solution of 1.80 g sodium nitrite in 5 ml of water was run into the above mixture after cooling with ice. The diazo solution was removed from the ice and set aside for 20-30 minutes. The excess of nitrous acid was decomposed by urea. After dilution with 50 ml of water, sodium acetate (about 12 g) was added to the diazo solution until it gave a neutral reaction with congo. The solution was filtered clear and ice water was added until its volume was 250 ml. For separate reactions with vinyl ethers, we took 50 ml portions of this solution. The remaining diazo solution served as a control; it underwent no change under the reaction conditions.

Azo-coupling of ethyl vinyl ether. 0.36 g ethyl vinyl ether, purified by distillation over sodium, was added to 50 ml solution of p-nitrodiazobenzene. A bottle containing the reaction mixture was periodically shaken and was cooled with ice. After only a few minutes, the solution reddened and an orange-red precipitate separated out. After 3-4 hours, the appearance of the mixture did not change; the solution was left overnight in ice. The precipitate was filtered off, washed with water and dried in a desiccator. The yield of crude p-nitrophenylhydrazone glyoxal was 0.80 g (83%). The resinous impurities were removed by treatment with a small quantity of benzene. For further purification water was run with stirring into the hot solution of the hydrazone in mixture with methyl alcohol and a small quantity of benzene until the start of crystallization. After separation of the benzene layer and cooling, threadlike light-orange crystals separated out from the aqueous solution. They were filtered off, washed and dried. They melted at 196° (with decomp.).

Found %: C 49.82, 49.77; H 3.77, 3.87. $C_8H_7O_3N_3$. Calculated %: C 49.73; H 3.65.

Glyoxal p-nitrophenylhydrazone was readily soluble in acetone, difficultly — in water, ether and benzene.

From 0.10 g crude azo-coupling product and p-nitrophenylhydrazine in methyl alcohol solution we obtained 0.15 g (88%) of glyoxal p-nitrophenylosazone. After recrystallization from pyridine, the osazone melted at 308° (with decomp.). The literature data give : m.p. 311° [3], 308° [4].

We added 4 ml hydrochloric acid (1 : 3) to a solution of 0.10 g of the p-nitrophenylhydrazone of glyoxal in 10 ml of methyl alcohol. The mixture was boiled for 1 hour. Upon cooling, the red precipitate of the osazone was filtered off, washed with aqueous methyl alcohol and ether. We isolated 0.07 g (82%) of the p-nitrophenylosazone of glyoxal. It melted at 309° (with decomp.).

Azo-coupling of methyl vinyl ether. 50 ml of p-nitrobenzenediazonium hydroxide solution and a one and one half fold excess of methyl vinyl ether were taken for the reaction. By the same method we isolated 0.88 g (91%, on the basis of the diazo compound taken) of the p-nitrophenylhydrazone of glyoxal. The product was purified as the previous one. It melted at 197° (with decomp.). The compound gave no melting point depression in a test mixture with the previously obtained glyoxal p-nitrophenylhydrazone.

Azo-coupling of n-butyl vinyl ether. 50 ml of a solution of p-nitrobenzenediazonium hydroxide and 0.55 g of n-butyl vinyl ether, purified by distillation over sodium, were taken for the reaction. By the same method we obtained 0.79 g of crude azo-coupling product in the form of a dark red powder. Purification was carried out as in the previous experiment with the exception that the solution of the hydrazone in methyl alcohol was boiled with activated carbon. The product was in the form of light brown crystals. It melted at 196° (with decomp.). The compound showed no melting point depression when a sample was mixed with the nitrophenylhydrazone of glyoxal; the action of p-nitrophenylhydrazine yielded the corresponding osazone.

SUMMARY

It was shown that the methyl vinyl, ethyl vinyl and n-butyl vinyl ethers react with p-nitrobenzenediazonium hydroxide in neutral aqueous medium.

In all cases the same p-nitrophenylhydrazone of glyoxal was formed as the result of the azo-coupling reaction. When heated with hydrochloric acid in methyl alcohol this hydrazone suffers dismutation with the formation of glyoxal and the osazone of glyoxal.

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ALKYLATION OF DIPHENYL WITH ALCOHOLS IN THE PRESENCE OF BF$_3$

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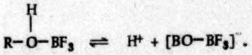
Diphenyl is used in admixture with other substances under the name of "Dowtherm" as an efficient heat-transfer medium [1]. To us the use of the alkyldiphenyls seems to be more practical — they being oily liquids with high boiling points and low freezing points. In a previous paper [2] one of us proposed the alkylation of diphenyl with alcohols in the presence of phosphoric acid; however, with this method the alkyldiphenyls are obtained in yields not exceeding 60% and the alkylation reaction requires 10 to 20 hours. We attempted to find a more efficient catalyst. In recent years many papers have appeared on the special role played by BF$_3$, having been used for many chemical processes (polymerization, alkylation, condensation, etc.). Judging from literature data [3], for many processes BF$_3$ is a more vigorous catalyst than either sulfuric acid or anhydrous aluminum chloride. Together with this, it fails to evoke undesirable side reactions, like, for example, oxidation or profound destructive changes, which take place when aluminum chloride is used.

In this paper we studied the alkylation of diphenyl with ethyl, n-propyl, isopropyl, n-butyl, isobutyl, isoamyl and hexyl alcohols. Since the alkylation of diphenyl with alcohols in the presence of BF$_3$ is not described in the literature, we began with a development of the method and the finding of the optimum conditions for this process. Both the temperature and the reactant proportions were varied. The conditions were found under which the highest yields of the alkyldiphenyls were obtained. It was established that in the alkylation of diphenyl it is expedient to run the reaction in two stages: 1) saturation of the starting alcohol with the boron fluoride under ice-cooling, and 2) heating of the thus obtained molecular compound with diphenyl under vigorous stirring; under these conditions the alkyldiphenyls are obtained in yields of 74-98%, based on starting diphenyl. For the most part the monoalkyl- and dialkyldiphenyls are formed in nearly equal amounts. In all cases oily substances were obtained, boiling without decomposition in the range 281-330%. These substances possess low freezing points (−42 to −70°), are quite viscous, fail to be oxidized when kept in the air for long periods of time, and are stable to oxidizing agents. Thus, they remain completely unchanged even after 50-hour heating with either chromic anhydride or potassium permanganate solution. Five percent nitric acid oxidizes them in sealed tubes only after 30 to 40-hour heating at 170°; here terephthalic acid is obtained, which indicates the entrance of the radicals in the para-position.

The purest substances and the highest yields are obtained in the alkylations with the normal alcohols. The reaction with them requires a longer heating period (2 stages) of up to 2-3 hours, but here the substances are obtained almost free of olefinic polymers, while with the iso-alcohols the obtained oils contain high-molecular polymers, from which it is difficult to effect separation by ordinary distillation. From this we conclude that the olefins of normal structure are polymerized with greater difficulty, and the alkylation with them proceeds more smoothly. We were unable to effect alkylation with the tertiary alcohols, since here even in the first stage, i.e. in the reaction of the alcohol with BF$_3$ the alcohol suffers decomposition, and the resulting olefins are rapidly polymerized into a gel-like mass, which fails to alkylate diphenyl under all conditions (when heated in an oil bath and even when heated in sealed tubes in an autoclave). When the substances are analyzed for carbon and hydrogen the values obtained for the hydrogen are somewhat high, and in some cases for the carbon also. This is explained by the fact that the substances contain traces of the fluoborate, which with glass at elevated temperature forms SiF$_4$, collecting as a white deposit at the end of the combustion tube. It can be assumed that it is also partially entrapped in the absorption apparatus. The molecular weights of all of the substances were determined cryoscopically, and also their specific gravities, refractive indices and freezing points. The data are summarized in the table.

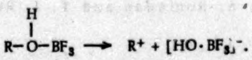
The mechanism of the alkylation of aromatic hydrocarbons with alcohols in the presence of BF$_3$ is discussed in several papers. Kenne and Sowa [4] believe that boron fluoride forms a molecular compound with the alcohol of type $ROH \cdot BF_3$, which suffers cleavage with the formation of olefins, being the alkylating agents.

Price and Lund [5] assume that BF_3 forms a molecular compound with the alcohol, finding itself in the equilibrium:



$$R-\overset{\overset{\displaystyle H}{|}}{O}-BF_3 \rightleftharpoons H^+ + [BO-BF_3]^-.$$

The cleavage into ions proceeds later:



$$R-\overset{\overset{\displaystyle H}{|}}{O}-BF_3 \longrightarrow R^+ + [HO \cdot BF_3]^-.$$

The alkyl cation formed here is the active alkylating agent. Such a mechanism best explains those alkylations in which the alcohols are incapable of forming olefins, as for example, benzyl alcohol.

To determine the nature of the mechanism of the studied reaction we ran the following experiment: BF_3 was passed into boiling isoamyl alcohol, the color of the alcohol gradually changed from light yellow to brown; after 3.5 hours stormy ebullition was observed, drops of water collected on the sides of the flask, and the liquid separated into 3 layers: 1) top layer – 0.6 of the total volume – light brown in color, 2) middle layer – 0.35 of the total volume – dark brown in color, and 3) bottom layer – aqueous, very slight – light yellow in color. All of the layers show acid reaction, and the two upper layers decolorize bromine water and represent mobile oily liquids; the middle layer has a pleasant odor. Vacuum-distillation of the top layer gave three fractions, when studied proving to be isoamylene polymers. The middle layer with b.p. 102-103° (30 mm), reddish-brown liquid; after distillation it fails to decolorize bromine water. This is the molecular compound, formed between the alcohol and the boron fluoride, and when distilled at atmospheric pressure it decomposes at 145-150° with the evolution of BF_3. By analysis it was established that it is a compound answering to the general formula $2ROH \cdot BF_3$. Such a relationship is confirmed by the fact that when the alcohol is saturated with boron fluoride a definite amount of BF_3 is always absorbed by a definite amount of the alcohol, which was established by weighing. A similar phenomenon was observed for all of the other alcohols.

From this we conclude that under the studied conditions the alkylation proceeds via the compound $2ROH \cdot BF_3$, which when decomposed forms olefins. As a result, under our experimental conditions the mechanism postulated by J. M. Kenne [4] is confirmed. In contrast to him, we obtain the complex $2ROH \cdot BF_3$ instead of $ROH \cdot BF_3$. This is in good agreement with the fact that simple ethers are formed, which was established in all of our observed reactions. Apparently, the formation of the simple ethers is linked with the intermediate boron etherates, which can suffer decomposition in accord with the scheme:

$$2(CH_3)_2CHCH_2CH_2OH \cdot BF_3 \longrightarrow [(CH_3)_2CHCH_2CH_2]_2O \cdot BF_3 + H_2O \cdot BF_3.$$

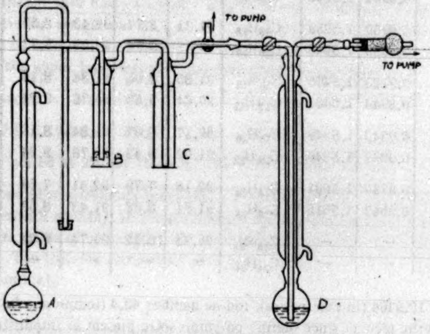
The B–O bond in the etherates is unstable [3], for which reason dissociation takes place, accompanied by the evolution of BF_3:

$$[(CH_3)_2CHCH_2CH_2]_2O \cdot BF_3 \longrightarrow [(CH_3)_2CHCH_2CH_2]_2O + BF_3.$$

We made an interesting observation with respect to the decomposition of the molecular compound that is formed between the alcohols and BF_3. Thus, independent of the alcohol, stormy ebullition of the mass (2nd stage of the operation) always begins within certain temperature limits, and specifically between 162-165°. It would seem to us that the decomposition temperature of the molecular compound should depend on the character of the alcohol, but the above fact was confirmed by us without equivocation in all of the discussed alkylations. This gives basis to postulate that the decomposition temperature depends on the character of the bond between the alcohol molecule and BF_3.

EXPERIMENTAL

An analytical grade of diphenyl and calcium fluoride was used; 100% sulfuric acid was prepared by addition of fuming sulfuric acid to concentrated sulfuric acid. Boric anhydride was prepared by calcining boric acid in a muffle furnace with subsequent grinding in a mortar. The alcohols were previously dried over potash and distilled over metallic sodium. Saturation of the alcohol with boron fluoride was performed in the apparatus (figure). The materials for the preparation of BF_3 were placed in flask A – 17.55 g B_2O_3 was dissolved with mild heating in 136 ml conc. H_2SO_4. 55.5 g previously dried CaF_2 was added to the cooled solution. This mixture was heated over wire gauze and the temperature was gradually raised to 300°. The BF_3 which formed was passed through wash bottle B, in which was placed 20 ml 100% H_2SO_4 and 5 g B_2O_3. The dried and purified BF_3 was sucked through an empty safety bottle C by a water-jet pump into reaction flask D containing alcohol which was immersed in an ice mixture. The experiments showed that the most complete absorption of BF_3 by alcohol took place upon passage of 8-10 bubbles per minute. The rate of introduction was regulated by intensity of heating of flask A. Saturation occured slowly in the course of 3-5 hours. The alcohol at first yellowed slightly and towards completion of the reaction had a brownish hue. The temperature in flask D rose to 40-45° during the reaction, which indicated a chemical process was taking place.



Apparatus for alkylation in the presence of BF_3. Explanation in text.

After the reaction was complete, introduction of BF_3 was stopped, flask D was closed off with the aid of glass stopcocks and left to stand overnight. The compound we thus obtained was then transferred to a flask connected to reflux condenser and mechanical stirrer. 25 g diphenyl was added through an opening in the side of this flask; the reaction mixture was heated on an oil bath with vigorous stirring. No visible changes occurred until the temperature of the oil bath reached 165-170° (162-165° in the reaction mixture). Only when this temperature was reached did a vigorous evolution of BF_3 begin in the form of bluish fumes which evolved and were absorbed by anhydrous alcohol. The reaction mixture vigorously boiled at this point and the surface of the flask and reflux condenser became covered with drops of water which copiously dripped back down. Alkylation began at this time as indicated by the formation of oily drops on the surface of the liquid. The violent boiling ceased after 2-3 minutes and the remainder of the reaction went smoothly. Heating at 165-170° was continued from 30 minutes to one and one half hours and for the normal alcohols – to 3 hours. The oily layer gradually increased. The cooled reaction mass was diluted with water, the upper oily layer was treated with steam to remove the unreacted diphenyl and olefin polymers. The olefins were collected in a receiver in the form of a light oil and the diphenyl congealed in the condenser. The undistilled oil was separated, dried over calcium chloride and then fractionated. Since the conditions described were optimal (yield up to 98%), they were maintained for the other alcohols.

Alkylation of diphenyl with isoamyl alcohol. In the course of the experiment it was observed that the absorption of BF_3 by alcohol was more intense when the reaction was performed with ice cooling. On the contrary, a comparatively high temperature was needed for the process of alkylation of diphenyl; therefore, after many experiments we devised the following method of alkylation in two stages. Taken: CaF_2 55.5 g, conc. H_2SO_4 135 ml, B_2O_3 17.5 g, isoamyl alcohol 40 g, diphenyl 25 g. Saturation of the alcohol with BF_3 was performed in the course of 5 hours with ice cooling. The increase in weight was about 18 g. The second stage entailed heating on an oil bath to 165-170° for one and one half hours. The yield of alkyldiphenyls was 98%, based on the diphenyl. We obtained 4 fractions at 765 mm: 1st — boiling range 298-305°, 2nd — boiling range 310-315°, 3rd — boiling range 340-345°, 4th — boiled above 345°. The fractions were transparent, almost colorless oils. Their greenish color intensified in passing from the 1st to the 4th fraction. The 3rd and 4th fractions visibly decolorized bromine water. Analysis showed them to be a mixture of alkyldiphenyls with high-molecular olefin polymers. The analytical data are given in the table.

Initial alcohol + diphenyl	Temperature		d_4^{20}	n_D^{20}	General formation	Found (in %)		Calculated (%)		M	
	boiled	solidified				C	H	C	H	found	calculated
Isoamyl	298-302°	—55°	0.8876	1.5075	$C_{17}H_{20}$	91.16	10.33	91.07	8.93	217.11	224.17
	310-313	—53	0.8976	1.5102	$C_{22}H_{30}$	89.74	10.31	89.79	10.21	293.4	294.22
Isobutyl	282-286	—51	0.9070	1.5295	$C_{16}H_{18}$	91.48	9.03	91.43	8.57	207.36	210
	306-308	—46	0.8952	1.5142	$C_{20}H_{26}$	90.35	9.81	90.23	9.77	259.76	266
n-Butyl	308-310	—70	0.8950	1.5259	$C_{16}H_{18}$	91.31	8.77	91.43	8.57	208.8	210
	324-326	—66	0.8939	1.5248	$C_{20}H_{26}$	90.45	9.94	90.23	9.77	264.6	266
Isopropyl	295-298	—55	0.9123	1.5475	$C_{15}H_{16}$	91.85	8.05	91.84	8.16	199.5	196
	315-316	—48	0.8949	1.5480	$C_{18}H_{22}$	90.84	9.55	90.76	9.24	243.0	238
n-Propyl	299-300	—48	0.9343	1.5349	$C_{15}H_{16}$	92.17	8.47	91.84	8.16	200.6	196
	328-330	—41	0.9297	1.5340	$C_{18}H_{22}$	91.02	9.43	90.76	9.24	236.0	238
Ethyl	281-282	—51	0.9793	1.5681	$C_{14}H_{14}$	92.18	7.79	92.31	7.69	182.3	182
	304-305	—50	0.9547	1.5615	$C_{16}H_{18}$	91.61	8.66	91.43	8.57	212.1	210
Hexyl	313-315	—	—	—	$C_{18}H_{22}$	90.78	10.12	90.74	9.24	240.7	238
	330-331	—	—	—	$C_{24}H_{34}$	—	—	—	—	314.0	322

Monoisoamyldiphenyl: η_{20} 12.9164 (in centipoises), iodine number 43.4 (iodine numbers were determined in order to establish the purity of the product since olefin polymers were present as impurities). Nitration was carried out according to Hubner and Luddens [6]. We obtained the mononitro derivative of diisoamyldiphenyl.

Found %: N 4.05. $C_{22}H_{29}O_2N$. Calculated %: N 4.12.

We carried out the oxidation of diisoamyldiphenyl, boiling range 310-315° at 765 mm, 150-152° at 2 mm with 7% nitric acid in sealed tubes with heating up to 170° for 12 hours. We obtained two acids: p-diphenylcarboxylic, m.p. 226° (literature data [7] for p-diphenylcarboxylic acid give m.p. 229°) and terphthalic which sublimed above 300°.

Alkylation of diphenyl with isobutyl alcohol was performed by the same method. The same amounts of reagents were taken for the preparation of BF_3: 25 g of diphenyl, 40 g of isobutyl alcohol (b.p. 107-108°, d_4^{20} 0.8031, n_D^{20} 1.3960). The addition in weight (upon weighing before and after saturation with BF_3) was accounted for in all the condensations. It amounted to 18.28-18.40 g for 40 g of alcohol. The duration of heating on the oil bath was different in the second stage of the experiment. It was found that an hour and a half of heating fully sufficed for the completion of the reaction. If heating was further prolonged (to 4-5 hours in our experiments), the yield of isobutylene isomers definitely increased. We isolated mono- and dibutyldiphenyls — transparent oils with a faintly visible greenish hue. The yield was 88%.

Monoisobutyldiphenyl: boiling range 282-286°, η_{20} 16.89, σ_{15} 30.96, iodine number 18.2.

Diisobutyldiphenyl was nitrated.

Found %: N 4.21. $C_{20}H_{25}O_2N$. Calculated %: N 4.49.

Alkylation of diphenyl with n-butyl alcohol (b.p. 117-118°, d_4^{20} 0.8094, n_D^{20} 1.3908). The ratio of the reagents was the same. Heating was for 2-3 hours on an oil bath. We obtained 2 fractions: 1st — b.p. 308-310° at 764 mm, 2nd — b.p. 324-326°. The yield of mono- and dibutyldiphenyls was 100%. These were the purest oils, free of olefins and had low solidification points (—66 to —70°).

Alkylation of diphenyl with isopropyl alcohol (b.p. 81-83°, d_4^{20} 0.7885, n_D^{20} 1.3964). The ratio of reagents and the method were the same. Steam distillation yielded 0.450 g of unchanged diphenyl. We obtained a 74% yield of mono- and diisopropyldiphenyls. They were transparent yellow oils.

Monoisopropyldiphenyl: b.p. 295-298°, η_{20} 18.94.

Alkylation of diphenyl with n-propyl alcohol (b.p. 97-98°, d_4^{20} 0.8031, n_D^{20} 0.3826). Alkylation was performed with heating for 4 hours. We obtained 2 fractions: 1st – b.p. 299-300° at 757 mm, 2nd – b.p. 328-330°. The total yield was about 100%. We obtained relatively pure mono- and dipropyldiphenyls as shown by analysis. They boiled within narrow ranges.

Monopropyldiphenyl: b.p. 299-300°, η_{20} 27.84, σ_{15} 32.20, iodine number 21.8.

Alkylation of diphenyl with ethyl alcohol. Anhydrous alcohol was used. Heating (2 stages) was for 6 hours. Diphenyl was not separated. There was a strong odor of ethyl alcohol upon alkylation and it was collected in a cooled ampoule and identified. We obtained 2 fractions: 1st – b.p. 281-282° at 768 mm, 2nd – b.p. 304-305°. The total yield was 85.3%. The mono- and diethyldiphenyls were transparent colorless oils.

Alkylation of diphenyl with hexyl alcohol. 80 g of hexyl alcohol was saturated with BF_3 for 6 hours with ice cooling. The addition in weight was 27.1 g. 107.1 g of the molecular compound was heated with 60 g of diphenyl over oil bath to 160-170° for 3 hours. Decomposition of the molecular compound occurred at 159-162°. After usual treatment, the upper layer was distilled over metallic sodium.

We obtained 2 fractions: 1st fraction – b.p. 313-315° at 750 mm, 148-150° at 2 mm, σ 40.6.

Found %: C 90.78; H 10.12. M 240.7. $C_{18}H_{22}$. Calculated %: C 90.74; H 9.24. M 238.

The 2nd fraction boiled at 330° at 750 mm, 170-174° at 2 mm; M 314.

Hexyldiphenyls had been previously prepared by I. S. Pokrovskaya and R. Ya. Sushchik [8] by the reaction of hexyl bromide with diphenyl in the presence of $AlCl_3$. They prepared the mono-(2 isomer), di-(2 isomer) and trihexyldiphenyls in yields of up to 80%. We obtained only one monohexyldiphenyl and one dihexyldiphenyl in the presence of BF_3. The isolated compounds were pure oily products with a yellowish cast. Their yields, based on diphenyl, were theoretical.

SUMMARY

1. A method was developed for the alkylation of diphenyl with ethyl, n-propyl, isopropyl, n-butyl, isobutyl, isoamyl and hexyl alcohols.

2. It was established that the purest alkyldiphenyls, almost completely free of unsaturated compounds, are obtained when the alkylations are run with normal alcohols.

3. The diphenyl is alkylated at the moment when the molecular compounds of the alcohols with boron fluoride suffer decomposition (decomposition temperature 162-165°).

4. With BF_3 the alcohols form molecular compounds of the $2ROH \cdot BF_3$ type.

5. Both mono- and dialkyldiphenyls are obtained in the alkylations, with the former predominating.

6. The alkyldiphenyls obtained by us are oils with low freezing points and fairly viscous; they fail to decompose when distilled at atmospheric pressure and are stable to oxidizing agents.

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THE PREPARATION AND PROPERTIES OF N-ARYLMALEIMIDES

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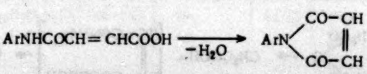
The N-arylmaleimides are slightly studied compounds and deserve attention from both the theoretical and practical viewpoints. In the literature it is indicated that they possess both insecticidal and fungicidal properties [1].

The N-arylmaleimides are best obtained by the cyclization of N-arylmaleamic acids in accord with the scheme:



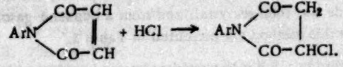
$$\mathrm{ArNHCOCH{=}CHCOOH} \xrightarrow[-H_2O]{} \mathrm{ArN}\begin{matrix}\mathrm{CO{-}CH}\\ \|\\ \mathrm{CO{-}CH}\end{matrix}$$

The cyclization of N-arylmaleamic acids can be regarded as being an intramolecular acylation reaction with the cleavage of water. As was to be expected, the indicated reaction proceeds only in the presence of water-removing substances. According to the literature, the latter function can be fulfilled by acetyl chloride, phosphorus pentoxide, phosphorus oxychloride, phosphorus trichloride, phosphorus pentachloride, thionyl chloride, acetic anhydride, etc.

Considerable amounts of side products are formed when the N-arylmaleamic acids are reacted with acetyl chloride [2], consequently, we rejected the use of acetyl chloride. N-Phenylmaleimide was obtained by heating N-phenylmaleamic acid with phosphorus pentoxide *in vacuo* at 250° [3]. There are other statements on the use of phosphorus pentoxide for cyclizing acids of the indicated type. Literature data, and also our studies, show that in the reaction of N-arylmaleamic acids with P_2O_5 the yields of the N-arylmaleimides are usually of the order of 50-60%. Piutti [4] used phosphorus oxychloride for the cyclization of N-arylmaleamic acids in organic solvents. The use of acetic anhydride for the cyclization is indicated in one of the patents [5]. Using acetic anhydride as a dehydration agent, Piutti came to the conclusion that the latter decomposes p-hydroxyphenylmaleamic acid into the acetyl derivative of p-aminophenol and maleic acid [4]. As a result, the data found in the literature on the cyclization of N-arylmaleamic acids are inadequate, and at times contradictory.

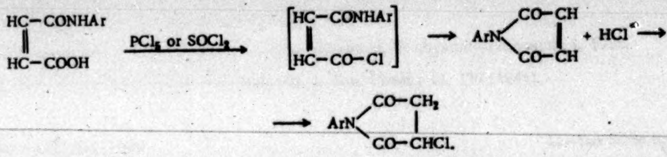
We used phosphorus pentoxide, phosphorus tri- and pentachlorides, thionyl chloride and acetic anhydride in the role of condensation agents. The cyclizations with phosphorus pentoxide were realized by fusing it with the N-arylmaleamic acids at 130-170°. The yields of the N-arylmaleimides were 50-60%.

The reaction with phosphorus trichloride was run in boiling xylene. We established that the N-arylmaleimides are formed under short heating at temperatures not exceeding 90°. Prolonged heating results in the reaction going further, and together with other compounds, the imide of chlorosuccinic acid is formed:



$$\mathrm{ArN}\begin{matrix}\mathrm{CO{-}CH}\\ \|\\ \mathrm{CO{-}CH}\end{matrix} + \mathrm{HCl} \longrightarrow \mathrm{ArN}\begin{matrix}\mathrm{CO{-}CH_2}\\ |\\ \mathrm{CO{-}CHCl.}\end{matrix}$$

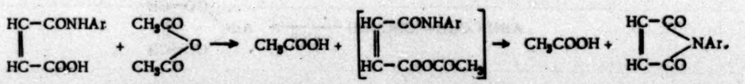
When the N-arylmaleamic acids are cyclized in the presence of either phosphorus pentachloride or thionyl chloride the imides of chlorosuccinic acid are formed in good yields by the postulated scheme:



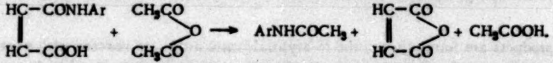
As intermediate products of the indicated reaction we attempted to isolate the acid chlorides of the N-arylmaleamic acids. However, we failed in this. Quite probably the acid chlorides are extremely unstable compounds, and their cyclization with the loss of HCl proceeds very rapidly.

We postulated that the acid chlorides of the N-arylmaleamic acids with negative substituents in the aromatic ring would be more stable. To confirm this we ran some special experiments with different N-arylmaleamic acids under extremely diverse temperature conditions, but still we were unable to isolate the acid chlorides. In all cases we obtained the N-arylamides of chlorosuccinic acids. The formation of the latter was shown by their identification with the reaction products of the N-arylmaleimides with hydrogen chloride in acetic acid medium.

When the N-arylmaleamic acids are cyclized with acetic anhydride under mild conditions the N-arylmaleimides are always obtained in excellent yield. The postulated reaction scheme is:



Under more drastic conditions, when boiled with excess acetic anhydride, acylation takes place with the formation of acetanilide or its derivatives, in accord with the scheme:



In some cases, for example with acetamidophenylmaleamic acid, the formation of the diacetyl derivative proceeds with great ease. A study of the cyclization reaction of N-arylmaleamic acids and the ease of formation here of N-arylmaleimides in good yields permits making the assertion that the N-arylmaleamic acids are the cis-isomers.

The method developed by us for the synthesis of N-arylmaleimides with the aid of acetic anhydride in the presence of sodium acetate is both general and fully accessible; this convenience is of great importance when it is considered that some of these syntheses find practical use. With the aid of this reaction we synthesized and studied some previously unknown N-arylmaleimides.

EXPERIMENTAL

Reaction of N-arylmaleamic acids with phosphorus pentoxide. 9.5 g N-phenylmaleamic acids was heated on an oil bath to 100-130° and 3 g of phosphorus pentoxide was added with stirring to the hot acid. After 4-5 minutes, the reaction began and was accompanied by a rapid temperature rise to 160-180° after which the reaction mass liquified. It solidified upon cooling. The melt was treated with water, filtered, dried and then extracted with benzene. The benzene extract was filtered free of precipitate, the imide was precipitated in the filtrate with gasoline and the dry imide was then recrystallized from a benzene-gasoline mixture. The data for the 3 imides which we synthesized by this method are presented in Table 1.

Reaction with phosphorous trichloride. 9.5 g N-phenylmaleamic acid was placed in a 3-necked flask fitted with stirrer, reflux condenser and dropping funnel and 150 ml dry xylene was added. The mixture was heated to a boil and 1.7 ml of PCl_3 was added drop-wise with stirring. The mixture was boiled for 5 minutes, then cooled and filtered; most of the solvent was driven off from the filtrate and gasoline was added to the concentrated solution of the imide. The imide which came down was crystallized from a benzene-gasoline mixture. It was in the form of yellow needles which melted at 88-89°. A test mixture of the compound with pure N-phenylmaleimide gave no depression.

TABLE 1

Name	Formula of imide	Yield (in %)	Melting point	Nitrogen content (in %)	
				found	calculated
N-Phenylmaleimide	$C_{10}H_7O_2N$	56	88-89°	7.9	8.1
N-p-Tolylmaleimide	$C_{11}H_9O_2N$	51	141-143	7.46	7.5
N-p-Methoxyphenylmaleimide	$C_{11}H_9O_3N$	51	148	7.08	6.9

TABLE 2

No.	Imides of chlorosuccinic acid	Formula	Melting point	Yield (in %)	Content (in %)			
					chlorine		nitrogen	
					found	calculated	found	calculated
1	N-Phenylimide	$C_{10}H_8O_2NCl$	118-119°	67	16.5	16.9	6.5	6.6
2	N-p-Tolylimide	$C_{11}H_{10}O_2NCl$	157	70	16.2	15.88	6.2	6.26
3	N-m-Tolylimide	$C_{11}H_{10}O_2NCl$	137-138	76	16.02	15.88	6.1	6.26
4	N-o-Tolylimide	$C_{11}H_{10}O_2NCl$	120-121	70	–	–	6.39	6.26
5	N-p-Ethoxyphenylimide	$C_{12}H_{12}O_3NCl$	125	68	13.7	14.00	5.4	5.5
6	N-p-Methoxyphenylimide	$C_{11}H_{10}O_3NCl$	142-143	71	–	–	6.0	5.88
7	N-m-Nitrophenylimide	$C_{10}H_7O_4N_2Cl$	145-146	79	14.28	13.9	10.86	11.00
8	N-p-Nitrophenylimide	$C_{10}H_7O_4N_2Cl$	173-174	84	13.7	13.9	11.26	11.00

TABLE 3

Name	Formula	Melting point	Yield (in %)	Content N (in %)	
				found	calculated
Acetanilide	C_8H_9ON	113-114°	74	10.46	10.36
m-Acetotoluidide	$C_9H_{11}ON$	64-65	75	9.50	9.38
p-Acetanisidide	$C_9H_{11}O_2N$	126-127	70	8.29	8.48
o-Chloroacetanilide	C_8H_8ONCl	87-88	73	8.3	8.26
p-Chloroacetanilide	C_8H_8ONCl	175-176	76	8.1	8.26

When the same quantities of reagents were boiled for a longer period of time (40-45 minutes), a yield of up to 30% was obtained of a white crystalline compound which melted at 118-119°; it was the imide of chlorosuccinic acid.

Found %: N 7.0, 6.7 (Kjeldahl); Cl 16.7 (Volhard). $C_{10}H_8O_2NCl$. Calculated %: N 6.6; Cl 16.9.

Reaction of N-arylmaleamic acids with phosphorus pentachloride and thionyl chloride. 9.6 g N-phenylmaleamic acid, heated to 35-40°, was mixed with 11.5 g of phosphorus pentachloride. The reaction proceeded rapidly and the temperature rose to 75°. After cooling, the congealed mass was washed with water until there was no acid reaction with congo. The dried product was recrystallized from a benzene-gasoline mixture. Several imides of chlorosuccinic acid were obtained by this method with certain modifications. The data on them is given in Table 2 (Compounds 1-6). The composition of the prepared imides of chlorosuccinic acid was confirmed by analysis and comparison with the compounds synthesized from N-arylmaleimides and HCl (mixing tests).

Thionyl chloride reacts in the same manner as phosphorus pentachloride with N-arylmaleamic acids. 5 ml $SOCl_2$ was added with stirring to 5.7 g of N-phenylmaleamic acid. The reaction went at room temperature in the course of 10-15 minutes. The reaction mass was poured into a small porcelain cup and left exposed until complete escape of SO_2 and HCl. The solidified crystalline mass was recrystallized from benzene. We obtained a white crystalline substance, m.p. 117-118°. Its yield was 5.2 g (83%). A test mixture with the N-phenylimide of chlorosuccinic acid gave no melting point depression. At −10° and after 2 hours of reaction, the yield was 87%.

Found %: N 6.89; Cl 16.3. $C_{10}H_8O_2NCl$. Calculated %: N 6.68; Cl 16.90.

The reaction with $SOCl_2$ also yielded the m- and p-nitrophenylimides of chlorosuccinic acid. The reaction was performed at 12-15° for 1 and 2 hours. The data are given in Table 2 (Compounds 7 and 8).

In order to identify the compounds isolated, the already cited N-arylimides of chlorosuccinic acid were synthesized concurrently by the reaction of N-arylmaleimides with hydrogen chloride.

TABLE 4

Name	Formula	Temperature	Yield (in %)	Melting point	Analysis			
					N (in %)		molecular weight	
					found	calculated	found	calculated
N-o-Methoxyphenylmaleimide	$C_{11}H_9O_3N$	50-60°	79	119-120°	6.68	6.89	205.1 203.8	203.2
N-o-Chlorophenylmaleimide	$C_{10}H_6O_2NCl$	40	80	59-60	6.95 6.88	6.75	209.0 200.0	207.6
N-p-Chlorophenylmaleimide	$C_{10}H_6O_2NCl$	75-80	79	109-110	6.96 6.95	6.75	210.6 202.0	207.6
N-β-Naphthylmaleimide	$C_{14}H_9O_2N$	65-70	92	154-155	6.45 6.38	6.28	228.8	223.2
N-p-Benzeneazophenylmaleimide	$C_{16}H_{11}O_2N_3$	75	85	160-161	15.2 14.95	15.15	270.5	273.3
N-2,5-Dichlorophenylmaleimide	$C_{10}H_5O_2NCl_2$	40	88	109-110	5.95 5.79	5.79	237.5 240.0	242.1
N-2,4,5-Trichlorophenylmaleimide	$C_{10}H_4O_2NCl_3$	60	82	104	5.20	5.06	281.3 271.3	276.5
N-4-Chloro-2-nitrophenylmaleimide	$C_{10}H_5O_4N_2Cl$	65	90	169	11.30	11.17	250.4 249.4	252.6
N-2-Nitro-4-ethoxyphenylmaleimide	$C_{12}H_{10}O_5N_2$	40	87	83	11.01 10.80	10.75	258.5	262.6
N-3-Nitro-4-tolylmaleimide	$C_{11}H_8O_4N_2$	53-55	86	102	12.27	12.06	228.3	232.2
N-5-Nitro-2-tolylmaleimide	$C_{11}H_8O_4N_2$	65	90	167-168	12.1	12.06	230.0 227.8	232.2
N-4-Chloro-2-tolylmaleimide	$C_{11}H_8O_2NCl$	25	91	68	6.38	6.32	218.0	221.5
N-4-Acetamidophenylmaleimide	$C_{12}H_{10}O_3N_2$	70	84	166	12.12 12.37	12.17	–	–

Reaction of N-arylmaleamic acids with acetic anhydride under harsh conditions. 0.02 mole of N-arylmaleamic acid was boiled with 0.08 mole of acetic anhydride for 1-1.5 hours. The reaction mass was then poured into a beaker with water and the liquid was brought to a boil; the excess of anhydride hydrolyzed and upon cooling the solution, a white crystalline precipitate of acetanilide fell down. Several acetanilides, listed in Table 3, were synthesized by this method.

Reaction of N-arylmaleamic acids with acetic anhydride under mild conditions. 1 g sodium acetate and

0.09 mole acetic anhydride were added to 0.03 mole N-arylmaleamic acid. The reaction mixture was heated on a water bath, while stirring, from 40 to 80° depending on the rate of reaction and held at this temperature from 20 to 40 minutes. After cooling, the reaction mass was poured on ice. The insoluble precipitate of the imide was filtered off, washed, dried and recrystallized from a benzene-gasoline mixture. We obtained the N-arylmaleimides by this reaction. The reaction conditions, properties and analytical data for the compounds isolated are presented in Table 4.

A characteristic property of acet-p-phenylmaleimide is the exceptional ease of displacement of the maleic radical with acetic anhydride and the subsequent formation of diacet-p-phenylenediamine.

SUMMARY

1. The ease with which the N-arylmaleamic acids are cyclized indicates that they have the cis-isomer structure.

2. As the result of the intramolecular cleavage of water in the action of P_2O_5 on N-arylmaleamic acids the corresponding imides are obtained in 50-60% yields.

3. In the reaction of the N-arylmaleamic acids with either PCl_5 or $SOCl_2$ the end reaction products are the N-arylamides of chlorosuccinic acids.

4. Depending on the reaction conditions, the use of phosphorus trichloride for the cyclization leads to the formation of either the imides of the N-arylmaleamic acids or the imides of chlorosuccinic acid.

5. A simple method was developed for the preparation of N-arylmaleimides by reacting the appropriate acid with acetic anhydride in the presence of sodium acetate.

6. Thirteen new N-arylmaleimides and 6 new N-arylamides of chlorosuccinic acid were synthesized and their properties studied.

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1.00 mole acetic anhydride were added to 1.25 mole N-arylanthranilic acid. The reaction mixture was heated on a water bath, while stirring, from 40 to 80° [illegible] from 70 to 80 minutes. After cooling, the reaction mass was poured [illegible] of the [illegible] was filtered off, washed, dried and [illegible] N-arylanthranilic [illegible] the reaction. The constants [illegible] data for the compounds isolated are presented in Table 4.

A characteristic property of acyl-p-phenylene [illegible] the [illegible] radical with which [illegible] and the subsequent [illegible].

SUMMARY

1. The ease with which the N-arylanthranilic acids [illegible] structure.

2. As the result of the intramolecular cleavage of water in the course of [illegible] N-arylanthranilic acids the corresponding [illegible] are obtained in 50-95% yields.

3. In the [illegible] of the N-arylanthranilic acids with either PCl₅ or SOCl₂ the end reaction products are the N-aryl[illegible] of the corresponding acids.

4. Depending on the reaction conditions, the [illegible] the formation of [illegible] of the N-arylanthranilic acids [illegible] acid.

5. A simple method was developed for the [illegible] of N-aryl[illegible] by reacting the anthranilic acid with [illegible] in the presence of sodium [illegible].

6. Thirteen new N-aryl[illegible] and 6 new N-aryl[illegible] of anthranilic acid were obtained and their properties studied.

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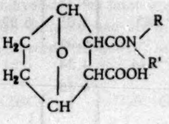
SYNTHESIS OF SOME 3,6-ENDOXOHEXAHYDROPHTHALIC ACID DERIVATIVES

N. N. Melnikov and V. A. Kraft

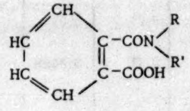
In recent years some of the 3,6-endoxohexahydrophthalic acid derivatives have found agricultural use as nonselective and selective herbicides and as defoliants, and also for the prepicking removal of leaves from the cotton and other plants [1-8]. In particular, the disodium salt of exo-cis-3,6-endoxohexahydrophthalic acid, obtained by the hydrogenation of the maleic anhydride adduct with furan [10-11], has found widespread use. The use of this compound for the removal of cotton leaves, with an expenditure norm of 1.5-2.0 kg per hectare, gives satisfactory results and accelerates the opening of the cotton boll [9]. However, a number of essential disadvantages are possessed by this compound, the most important of which are the comparatively high toxicity for humans and animals and the relatively short-lived effect, since in a short time after treating plants with this compound the cotton plant can develop secondary sprouting. In connection with the above it appears of interest to study the different derivatives of 3,6-endoxohexahydrophthalic acid for the purpose of obtaining compounds that are more active and show lower toxicity for humans and animals.

Despite the practical use of 3,6-endoxohexahydrophthalic acid in agriculture, a completely inadequate study of its derivatives and homologs has been made up to now. Only the dimethyl and diallyl esters of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids, and some of the acid esters, salts and imides of these acids, have been described in the literature [12-17]. Some of the bromo-3,6-endohexahydrophthalic acids are also described in the literature [18-23].

Of the 3,6-endoxohexahydrophthalic acid derivatives it appeared of first interest to synthesize the alkyl- and aryl-3,6-endoxohexahydrophthalamic acids (I), since the arylphthalamic acids (II), close to them in structure, show high physiological activity with respect to a large number of plants and some of them have found use as selective herbicides [24, 25]:

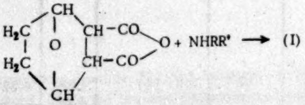


(I)



(II)

We obtained the alkyl- and aryl-3,6,-endoxohexahydrophthalamic acids by reacting the appropriate anhydride with an amine in an organic solvent:



Secondary amines form the corresponding quite stable 3,6-endoxohexahydrophthalamic acids in excellent yields, while the aryl-3,6-endoxohexahydrophthalamic acids are unstable when heated, and even during recrystallization, are easily converted into aryl-3,6-endoxohexahydrophthalimides. The corresponding derivatives of 3-methyl-3,6-endoxohexahydrophthalic acid were synthesized in similar manner, which in their properties approximate the 3,6-endoxohexahydrophthalic acid derivatives. The compounds obtained by us are given in Table 1.

TABLE 1

Substance	Starting substances (in g moles)		Yield (%)	Melting point	Nitrogen Analysis (%)*		Molecular Weight Determination**	
	Anhydride	Amine			Found	Calc.	Found	Calculated
N-Alkyl-(aryl)-3,6-endoxohexahydrophthalamic acids:								
N,N-Diethyl	0.025	0.025	84.6	132–133°	5.70 5.70	5.81		
N-Phenyl	0.01	0.0095	100	161 with decomp.	5.6 5.65	5.36	257.1 255.4	261.2
N-α-Naphthyl	0.005	0.0048	83.3	164	4.82 4.50	4.50	310.6 308.0	311.0
N-Arylimides of 3,6-endoxohexahydrophthalic acids:								
N-Phenylimide	0.01	0.01	100	163–164	5.74 5.98	5.76	Neutral	
N-α-Naphthylimide	0.05	0.05	100	219–220	5.25 5.08	4.77	Neutral	
N-Alkyl-(aryl)-3-methyl-3,6-endoxohexahydrophthalamic acids:								
N,N-Dimethyl	0.1	0.1	100	122–123	6.36 6.46	6.16		
N,N-Diethyl	0.1	0.1	90.2	129–130	5.69 5.43	5.49		
N-Phenyl	0.01	0.01	85.2	144–145	5.05 5.03	5.09	268.4 270.3	275.0
N-α-Naphthyl	0.01	0.0098	77.8	143.5–144	4.24 4.36	4.31	318.1 321.2	325.4
N-Phenylimide of 3-methyl-3,6-endoxohexahydrophthalic acid	0.01	0.01	100	179.5–180	6.29 6.07	5.83	Neutral	
N-Alkyl-(aryl)-4,5-dichloro-3,6-endoxohexahydrophthalic acids:								
N,N-Diethyl	0.005	0.005	57.7	146–147	4.85 4.42	4.52		
N-Phenyl	0.005	0.0047	100	186***	4.03 4.24	4.24	319.2 324.5	330.2

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* The nitrogen content was determined by the Kjeldahl method.

** The molecular weight was determined by titration.

*** The capillary was placed in the apparatus previously heated to 15° below the melting point.

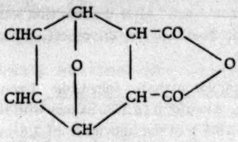
TABLE 2

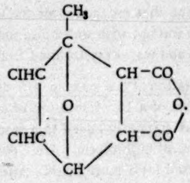
Name	Starting Substances (in g-moles)		Yield (%)	Melting Point	Molecular Weight Determination	
	Anhydride	Alcohol			Found	Calculated
Esters of 3,6-endoxohexahydrophthalic acid:						
Dipropyl	0.05	0.105	73.5	55–56°	269.7,268.6	270.0
Diisopropyl	0.05	0.15	59.0	103–104	269.0,266.5	270.0
Dibutyl	0.05	0,105	73.5	61–62	297.8,295.0	298.0
Diisoamyl	0.1	0.21	89.0	86–87	324.8,325.6	326.0
Esters of 3-methyl-3,6-endoxohexahydrophthalic acid:						
Dipropyl	0.1	0.21	77.5	61–62	276.7,278.5	284.0
Diisopropyl	0.1	0.3	81.5	76.5–77.5	282.2,280.1	284.0
Dibutyl	0.1	0.21	83.5	43–44	311.4,313.1	312.0

Because we used the anhydrides of the exo-cis isomers for the synthesis of the aryl and alkyl-3,6-endoxohexahydrophthalamic acids and since the reaction was run under extremely mild conditions, the compounds that we obtained are also undoubtedly the exo-cis isomers of the endoxohexahydrophthalamic acids.

In connection with the statements existing in the literature on the higher herbicidal activity of the esters when compared with the free acids and their salts* we synthesized a number of previously unknown esters of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids. We prepared the esters from the anhydrides and the corresponding alcohols in the presence of small amounts of benzenesulfonic acid, with removal of the water formed in the reaction by azeotropic distillation with dichloroethane. The compounds obtained by us are given in Table 2. The testing of these compounds on the cotton plant, made by K. E. Ovcharov, revealed that they are practically devoid of activity.

Together with studying the carbonyl derivatives of the 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids, we also made a study of their halo derivatives. First we undertook a study of the 4,5-dichloro derivatives of the indicated acids, which we obtained by the direct chlorination in chloroform of the adducts of maleic anhydride with furan and sylvan. The compounds that we obtained are apparently the anhydrides of the 4,5-dichloro-exo-cis-3,6-endoxohexahydrophthalic (III) and 3-methyl-4,5-dichloro-exo-cis-3,6-endoxohexahydrophthalic (IV) acids:


(III)


(IV)

By analogy with the corresponding bromides [17-22], the high-melting products, apparently, have the trans-configuration for the halogens, while the low-melting products have the cis-configuration.

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* Thus, for example, the butyl and isopropyl esters of 2,4-D show a herbicidal activity that is 3-4 times that of the sodium salt of this acid.

EXPERIMENTAL

Preparation of the anhydrides of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids. Ordinarily, in order to prepare the anhydride of the exo isomer of 3,6-endoxohexahydrophthalic acid and its homologs, the corresponding anhydrides are hydrogenated in solutions of organic solvents in the presence of colloidal palladium [10-12]. It is possible to hydrogenate the salts of the acids in aqueous solution in the presence of Raney nickel [26, 27]. In the latter case, hydrogenation is performed under increased pressure. We hydrogenated the adducts of maleic anhydride with furan and sylvan over metallic palladium supported on metallic nickel by the method of A. S. Ginsberg and A. P. Ivanov [28]. Hydrogenation was performed in acetone as well as aqueous soda solution at room temperature and normal pressure. The completion of hydrolysis was determined by the quantity of hydrogen absorbed. When hydrogenation was complete, the catalyst was filtered off and washed with an organic solvent. The washed catalyst was again used for the next hydrogenation operation. In most cases, the catalyst was used consecutively for several operations without loss of activity. After acetone was driven off, the prepared anhydrides were recrystallized and their constants were determined: the anhydride of 3,6-endoxohexahydrophthalic acid melted at 116-117° and the anhydride of 3-methyl-3,6-endoxohexahydrophthalic acid – at 105-106°, which corresponded to the literature data for the exo isomers [10-12].

When hydrogenation was performed in aqueous soda solution, upon acidification of the solutions, the corresponding acids separated out and were further separated out in the form of anhydrides by treatment with acetyl chloride. The yield of hydrogenation products was almost quantitative.

Preparation of 3,6-endoxohexahydrophthalamic and 3-methyl-3,6-endoxohexahydrophthalamic acids.

These acids were prepared by the reaction of the anhydrides of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids with the corresponding amines in dioxane solution. The reaction proceeded upon simple mixing of the solution of the above compounds in dioxane with evolution of heat. The reaction products crystallized out upon cooling. The reaction is best performed with cooling since in the case of the primary amines, a rise in temperature will cause the formation of imides.

Separate experiments showed that prolonged heating of aryl-3,6-endoxohexahydrophthalamic acids caused water to split out in an almost quantitative yield of the corresponding 3,6-endoxohexahydrophthalimides. This was easily confirmed by titration with alkali. The aryl-3,6-endoxohexahydrophthalamic acids were quantitatively titrated with caustic soda in alcoholic or acetone solution in the presence of phenolphthalein since the corresponding imides were neutral.

For purification, the N-alkyl(aryl)-3,6-endoxohexahydrophthalamic acids were recrystallized from methyl or ethyl alcohol.

Preparation of the esters of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids. For 0.1 mole of anhydride, 0.2 g of benzenesulfonic acid and from 30 to 60 ml of dichloroethane were taken. Esterification was performed in an apparatus that automatically returned to the reaction flask the dichloroethane that escaped after the water separated out. After the reaction was complete, the reaction mixture was washed with water and soda and dichloroethane was driven off. Upon cooling, the residue crystallized and was recrystallized from benzene.

Preparation of 3,6-endoxo-4,5-dichlorohexahydrophthalic anhydride. Upon thorough stirring and cool- to 0-5°, 49 ml of a 15.7% solution of chlorine in chloroform (a 10% excess with respect to the stoichiometric quantity) was gradually added to a suspension of 16.6 g of the anhydride of 3,6-endoxotetrahydrophthalic acid in 60 ml of chloroform. After the entire amount of chlorine solution had been added, the reaction mixture was stirred for 3 more hours. After this period, the precipitate that came down was filtered off and washed with cold chloroform. The yield of product was 70.5%. After recrystallization from chloroform, it melted at 161-162°.

Found % Cl 29.64, 29.58. $C_8H_6O_4Cl_2$. Calculated % Cl 29.91.

Preparation of 3-methyl-3,6-endoxo-4,5-dichlorohexahydrophthalic anhydride. Under the conditions described in the previous section, 18 g of 3-methyl-3,6-endoxotetrahydrophthalic anhydride and 111 ml of 7% solution of chlorine in chloroform, after standing for one night, yielded after filtration 1.35 g of product which melted at 151-152° after recrystallization from benzene.

Found % Cl 27.78, 27.91. $C_9H_8O_4Cl_2$. Calculated % Cl 28.24.

After the chloroform was driven off, we isolated a substance which melted at 107°. Analysis showed the product to be 3-methyl-3,6-endoxo-4,5-dichlorohexahydrophthalic anhydride and, evidently, the cis isomer.

SUMMARY

1. For the purpose of studying their physiological activity on plants we synthesized a number of previously unknown esters of 3,6-endoxohexahydrophthalic and 3-methyl-3,6-endoxohexahydrophthalic acids.

2. A number of previously unknown aryl- and alkyl-3,6-endoxohexahydrophthalamic acids and their derivatives were also synthesized.

3. The chlorination of 3,6-endoxotetrahydrophthalic and 3-methyl-3,6-endoxotetrahydrophthalic anhydrides gave the previously unknown anhydrides of 3,6-endoxo-4,5-dichlorohexahydrophthalic and 3-methyl-3,6-endoxo-4,5-dichlorohexahydrophthalic acids.

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QUINOLINE DERIVATIVES. XII.

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We present in this paper some experimental material that serves as confirmation and further development of our previously published communications [1, 2].

I. Mutual Condensation of Acetylated Amines, Formaldehyde and Methyl Ethyl Ketone. Our method for the preparation of lepidine and its derivatives from acetylated aromatic amines has been described earlier [1, 2]. In accord with the mechanism for this reaction the replacement of acetone by another ketone can lead to the synthesis of difficulty available 3,4-dialkyl-substituted quinolines; thus Manske obtained 3,4-dimethylquinoline from o-aminoacetophenone and propionaldehyde in low yield, and also from aniline and the difficulty available 2-methyl-3-oxobutanone [3]. We established that 3,4-dimethylquinoline and its homologs are formed from acetylated arylamines, formaldehyde and methyl ethyl ketone under the conditions of our described reaction. 4-Ethylquinoline is also formed in small amounts, which can easily be removed by recrystallizing the product to a constant melting point.

II. Synthesis of Some Phenylquinolines from Arylamines and Cinnamaldehyde. Although α-acylated quinolines are comparatively available, still the existing methods for their preparation require further improvement. A characterization of the general methods for the preparation of α-phenylquinolines is given in the paper by N. S. Kozlov [4]. In this paper we studied the reaction of aromatic amines with cinnamaldehyde for the purpose of establishing its mechanism and to elucidate the possibility of using it for preparative purposes.

When we ran this reaction in hydrochloric acid medium, by the method of Doebner and Miller, we obtained only about 10% of the theoretical yield of α-phenylquinoline, while o-toluidine gave an insignificant yield, and complete tarring was observed when the anisidines were used. In sulfuric acid medium the variation described by Grimaux [5] gave the poorest result; Murman was able to achieve greater success in his synthesis of α-phenylquinoline in sulfuric acid medium, especially when he introduced an excess of aniline into the reaction and used sulfuric acid of variable concentration, and by using nitrobenzene as an oxidizing agent [6, 7]. When calculated on the cinnamaldehyde, Murman obtained up to 50% of the theoretical yield of α-phenylquinoline in the separate experiments, but when calculated on the aniline, the yield was approximately only 20% of the theoretical. However, the Murman method is not applicable for a number of aniline derivatives, for example, the anisidines, due to their tarring under these conditions.

We studied the synthesis of the α-phenylquinolines, both directly from cinnamaldehyde and certain amines and also from the anils of various aromatic amines, which made it possible to establish the mechanism for this reaction [1] and as a result of this to select the conditions giving the best yields of the α-phenylquinolines.

When cinnamylideneaniline is taken as the starting anil and p-anisidine is added to the reaction mixture, then the latter , being the more basic amine,displaces the aniline from the anil [8, 9], as a result of which, in accord with the presented scheme, α-phenylquinoline is formed. Depending on the degree of basicity, the other amines also react in similar fashion.

At elevated temperature in weakly alkaline medium the cyclization of the diene anils proceeds with the formation of γ-substituted quinolines [10, 11]. In this case γ-phenylquinolines are formed from the anils of cinnamaldehyde [1]. The experiments, summarized in Table 4, are preliminary, since the method can be improved, for example, by running the reaction in the medium of an inert gas.

EXPERIMENTAL

Syntheses from acetylated amines. Synthesis of 3,4-dimethylquinoline. We took 20 g of acetanilide and 20 ml methyl ethyl ketone. The first part of the synthesis was performed as for the preparation of 4,6,8-trimethylquinoline [2]. After hydrolysis of the unreacted acetanilide, the flask was cooled and a 40% solution of caustic soda was added until the solution gave a basic reaction and 100 ml of alcohol was added. The ferric hydroxide which came down was filtered off, 30 ml of concentrated hydrochloric acid was added to the filtrate and the quinoline base was precipitated by a saturated solution of potassium ferrocyanide [12]. After decomposition with 10% caustic soda solution, the oil that formed was extracted with ether, the ether was driven off and the quinoline base was distilled. We obtained 4.3 g (18.5%) of product which completely crystallized. After recrystallization from n-hexane, the 3,4-dimethylquinoline melted at 73-74°. The picrate melted at 217°.

Found %: N 8.85. $C_{11}H_{11}N$. Calculated %: N 8.91.

The syntheses of the homologs of 3,4-dimethylquinoline that are not described in the literature were performed in the same manner (Table 1).

TABLE 1

Properties of Certain Homologs of 3,4-Dimethylquinoline

Name of initial amine	Yield of quinoline base (%)	Temperature		
		boiled at	melted at	picrate melted at
Acetyl-p-toluidine	20	~300°	67°	236°
Acetyl-o-toluidine*	20.5	~295	56	225
Acetyl-m-xylidine*	32	–	89	210

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* Purified through the difficulty soluble hydrochloride salt.

3,4,6-Trimethylquinoline. Found %: Pt 25.81. $(C_{12}H_{13}N \cdot HCl)_2PtCl_4$. Calculated %: Pt 25.96. Found %: N 8.32. $C_{12}H_{13}N$. Calculated %: N 8.20.

3,4,8-Trimethylquinoline. Found %: Pt 24.73; H_2O 4.74 $(C_{12}H_{13}N \cdot HCl)_2PtCl_4 \cdot 2H_2O$. Calculated %: Pt 24.79; H_2O 4.58. Found %: N 8.09 $C_{12}H_{13}N$. Calculated %: N 8.20.

3,4,6,8-Tetramethylquinoline. Found %: Pt 24.01; H_2O 4.48 $(C_{13}H_{15}N \cdot HCl)_2PtCl_4 \cdot 2H_2O$. Calculated %: Pt 23.86; H_2O 4.40. Found %: N 7.70 $C_{13}H_{15}N$. Calculated %: N 7.57.

Syntheses of phenylquinolines. At first, experimental syntheses for phenylquinolines were conducted by the following scheme. A mixture of 14 g of aniline, 7 g of nitrobenzene and 45 g of crystalline orthophosphoric acid (98-99%) was heated on an oil bath for 2 hours. The temperature of the reaction was 130-140°. 25 g of freshly distilled cinnamaldehyde was then gradually added through a dropping funnel. When the reaction was complete, the mixture was boiled for 15-20 minutes in dilute hydrochloric acid (1 : 3), 50 ml of which was added. The nitrobenzene was driven off with steam. The solution was allowed to settle, decanted from the resin and alkalized with a saturated soda solution. The product was extracted with ether and distilled after its ethereal solution had been dried with potash. After recrystallization from alcohol, *a*-phenylquinoline melted at 81° and its picrate – at 187°. The experimental results are presented in Table 2. The data of the table show that the yields of phenylquinolines were higher than they were in a sulfuric acid, and even more so than in a hydrochloric acid medium.

Syntheses of phenylquinolines from anils of cinnamaldehyde. When the reaction was performed with anils, it was found that the maximum phenylquinoline yields were obtained when 2 moles of the amine was reacted together with the anil. The following scheme was devised as a result of this. 18 g of p-toluidine, 7 g of p-nitrotoluene and 30 g of crystalline orthophosphoric acid were placed in a 250 ml round-bottomed flask. The flask was placed in an oil bath (heated to 150°) and gradually, in the course of 30 minutes, 18 g of the anil of p-toluidine was added through the condenser. The reaction continued for 3 hours at 160-170°. Separation of the base was performed as in the previous case. The results of several experiments are given in Table 3.

Syntheses with various amines and anils. Experiment 1. 16 g of cinnamylideneaniline and 20 g of p-anisidine were reacted in the manner prescribed. We isolated *a*-phenylquinoline the picrate of which melted at 187°. Its yield was 5.6 g (35%).

TABLE 2

Yields of Phenylquinolines Prepared from Aromatic Amines and Cinnamaldehyde in Phosphoric Acid Medium

Amines	Taken (in g)	Yield of phenylquinolines (in %, on amine)
Aniline	14	23.5
p-Toluidine	16	23.0
o-Toluidine	16	9.3
m-Xylidine	18	15.0 •
p-Anisidine	18	17.6
o-Anisidine	18	9.0

• 6,8-Dimethyl-α-phenylquinoline is not described in the literature. It was a viscous oil that boiled at 330-350°. It did not form a picrate.

TABLE 3

Yields of Phenylquinolines Prepared from Anils of Cinnamaldehyde in Phosphoric Acid Medium

Initial compounds			Phenylquinolines	
Name	melting point	taken (in g)	yield (in %, on anil)	melting point (from alcohol)
Anil	107°	16	47.5	83
p-Methylanil	82	18	49.0	69
o-Methylanil	73	18	41.0	48
2,4-Dimethylanil	80	20	35.0	–
p-Methoxyanil	123	20	53.5	133

Experiment 2. 20 g of cinnamylidene-p-anisidine and 16 g of aniline were reacted. We isolated α-phenylquinoline, the picrate of which melted at 187° and gave no depression with the picrate of known α-phenylquinoline. Its yield was 4.5 g (26%, based on the anil). A similar result was obtained when the reaction was performed with the hydrochloride salts of the anils and amines in a fusion (200°) or in solvents.

Experiment 3. 18 g of cinnamylidene-p-toluidine and 15 g of o-toluidine were reacted. We obtained an oily product which partially crystallized upon standing and had a characteristic odor. It did not form a picrate. Its yield was 4 g (22%).

Syntheses of γ-phenylquinolines. 3 g of the m-methylanil of cinnamaldehyde was placed in a clean copper tube, 30 cm long, 1.5 cm in diameter with previously dried Al_2O_3 catalyst. The tube with its contents was placed in a combustion furnace and the temperature was brought to 400-450°. It was measured by a thermometer located between the inner wall of the furnace and the outer surface of the tube. Dry air was passed through the apparatus to secure a more complete volatilization of the product. The receiver, connected through an adapter, was cooled with ice. 2.40 g of crude product was obtained in the form of a crystalline compound which melted at 129°. The picrate, m.p. 207°, 40.6% yield, was obtained from alcoholic solution.

The melting point of the picrate, similarly prepared from the anil of cinnamaldehyde, was 225° which corresponded to that cited for the picrate of γ-phenylquinoline [13].

Found %: N 12.96. $C_9H_6NC_6H_5 \cdot C_6H_2(NO_2)_3OH$. Calculated %: N 12.90.

The experimental results on the preparation of γ-phenylquinolines are given in Table 4, the analytical results – in Table 5.

It is interesting to note that 8-methyl- and 6,8-dimethyl-α-phenylquinolines did not form picrates, evidently due to steric hindrances [14].

The devised method and the mechanism established for the formation of α-phenylquinolines made it possible to solve certain practical problems such as, for example, the synthesis of atophan with the aid of the previously difficultly obtainable 4-methyl-2-phenylquinoline or the synthesis of 8-amino-2-phenylquinolines from o-nitroarylamines.

M. V. Yakovleva participated in the experimental work.

TABLE 4

Yields of Picrates of γ-Phenylquinolines Prepared from Anils of Cinnamaldehyde

Anils	Melting point of the picrate of the anil*	Melting point of the picrate of the phenylquinoline	Yield of picrate (in % on crude product)
Anil	119°	225°	8.2
p-Methylanil	167	214	12.0
o-Methylanil	159	217	16.0
m-Methylanil**	158	207	40.6
2,4-Dimethylanil	160	215	21.0
p-Methoxyanil	177	197	15.0

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* The picrates of all the anils and γ-phenylquinolines except 4-phenylquinoline were not described in the literature.

** Acicular crystals, in the form of nodules, light yellow, m.p. 126°.

TABLE 5

Analysis of Picrates of γ-Phenylquinolines

Name of quinoline	Nitrogen (in %)	
	Found	Calculated
4-Phenyl-6-methylquinoline	12.37	12.50
4-Phenyl-8-methylquinoline	12.60	12.50
4-Phenyl-6,8-dimethylquinoline	12.20	12.12
Quinoline from m-toluidine *	12.63	12.50

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* A possible mixture of bases.

SUMMARY

1. A method was developed for the synthesis of quinolines from acetylated aromatic amines, formaldehyde and methyl ethyl ketone, being the most convenient of the known methods for the preparation of 3,4-dimethylquinolines.

2. It was established that when the synthesis of phenylquinolines from aromatic amines and cinnamaldehyde is run in phosphoric acid medium that the yields are greater than when it is run in either hydrochloric acid or sulfuric acid. The best yields (40-50%) were obtained in their direct synthesis from the anils.

3. Because of steric hindrance, the α-phenylquinolines that are substituted in the 8-position fail to form picrates.

4. In the preparation of α-phenylquinolines from the anils in acid medium the phenomenon of "reamination" can occur with substitution of the less basic amine by the more basic.

5. At elevated temperature in the presence of aluminum oxide the cyclization of the anils of cinnamaldehyde proceeds with the formation of γ-substituted quinolines, inasmuch as the mechanism of the reaction changes.

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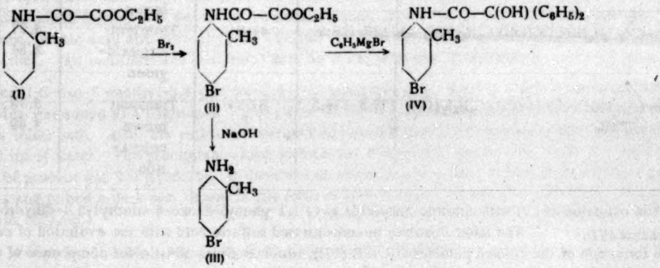
THE o-TOLUIDIDES OF DIARYLGLYCOLIC ACIDS AND THEIR TRANSFORMATION INTO 3,3-DIARYL-7-METHYLOXINDOLES. XXIV.

P. A. Petyunin and A. S. Pesis

H. Liebig [1] showed that when benzilic acid is heated with aromatic amines to 180-200° a mixture of high-molecular compounds of unknown structure is formed. In the experiment with the o-toluidide he isolated, together with the high-molecular compounds, a substance with m.p. 278°, which was postulated as being 3,3-diphenyl-7-methyloxindole.

Having studied the intramolecular condensation of the arylamides of hydroxycarboxylic acids, we decided to extend our information to the synthesis of the 3,3-diaryl derivatives of 7-methyloxindole and to compare our data for 3,3-diphenyl-7-methyloxindole (V) with the data of H. Liebig. Of the 3,3-diaryl derivatives of 7-methyloxindole only the 3,3-bis-(4'-methoxyphenyl)-7-methyloxindole [2] is described in the literature. To execute the assigned task we reacted ArMgX (Ar = C_6H_5-, p-$CH_3C_6H_4-$, o-$CH_3C_6H_4-$ and o-$CH_3OC_6H_4-$) with the ethyl ester of o-methyloxanilic acid to give a number of the o-toluidides of diarylglycolic acids. The properties and structure of the compounds obtained by us are shown in Table 1.

The 2-methyl-4-bromoanilide of benzilic acid (IV) was obtained by the following scheme:



The treatment of (I) with bromine gave the ethyl ester (II) of 2-methyl-4-bromooxanilic acid, which when heated with 30% sodium hydroxide solution gave the known 5-bromo-2-aminotoluene (III). The reaction of (II) with phenylmagnesium bromide gave (IV).

Under the influence of concentrated sulfuric acid the obtained diarylglycolic acid o-toluidides were transformed in good yields into the 3,3-diaryl derivatives of 7-methyloxindole (Table 2).

Liebig [1] gives a m.p. of 278° for (V), which is not confirmed by our data. Apparently, his substance had a different structure. The structure of (V) follows from its mode of synthesis, and is also supported by the following transformation:

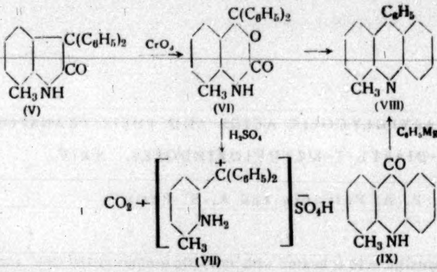
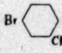


TABLE 1

Properties of o-Toluidides of Diarylglycolic Acids

No.	Formula	Melting point	Yield (%)	Coloration with Concentrated Sulfuric Acid	Nitrogen Content (%)	
					Found	Calculated
1	o-$CH_3C_6H_4NHCOC(OH)(C_6H_5)_2$ (X)	147-148°	45.3	Brown, going to green	4.50 4.70	4.40
2	o-$CH_3C_6H_4NHCOC(OH)(C_6H_4CH_3$-o)$_2$	148.5-150.5	62.8	Red-violet, going to a green	4.13 4.16	4.07
3	o-$CH_3C_6H_4NHCOC(OH)(C_6H_4CH_3$-p)$_2$	152.5-153.5	49.3	Red-violet, going to a yellow-brown	4.21 3.94	4.07
4	o-$CH_3C_6H_4NHCOC(OH)(C_6H_4OCH_3$-o)$_2$	128-128.5	41.9	Transient emerald-green	4.07 3.84	3.71
5	 NH−CO−C(OH)(C$_6$H$_5$)$_2$ (IV)	177.5-178.5	51.3	Transient brown coloration	3.79 3.49	3.53

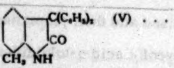
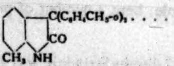
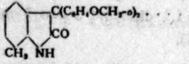
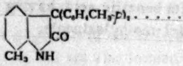
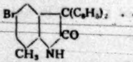
The oxidation of (V) with chromic anhydride gave 1,1-phenyl-3-oxo-5-methyl-3,4-dihydro-2,4,1-benzoxazine (VI). The latter dissolves in concentrated sulfuric acid with the evolution of carbon dioxide and the formation of the colored halochromic salt (VII), which is characteristic for compounds of this type [3]. The heating of (VI) in nitrobenzene medium gave 4-methyl-9-phenylacridine (VIII), which was isolated as the picrate. The structure of (VIII) was confirmed by the reverse synthesis, made according to Lemstedt [4]. Thus, the reaction of phenylmagnesium bromide with 4-methylacridine (IX) gave (VIII), the picrate of which proved to be identical with the above-described.

EXPERIMENTAL

Ethyl ester of 2-methyl-4-bromooxanilic acid (II). 16 g (0.1 mole) of bromine was added to a solution of 20.7 g (0.1 mole) of (I) (prepared by method [5]) in 100 ml of 80% acetic acid, and the reaction mixture was set aside for 1 hour at room temperature. Upon dilution with a three-fold volume of water, a heavy oily liquid separated out and rapidly crystallized upon slow stirring. Yield 22.8 g (80%). It was in the form of small rods (from alcohol), m.p. 101.5.

TABLE 2

Properties of 3,3-Diaryl Derivatives of 7-Methyloxindole

No.	Formula	Melting point	Yield (in %)	Analysis Data (in %)	
				found	calculated
1		254—255°	96.7	C 84.01, 83.79; H 5.72, 5.71; N 4.93, 4.69	C 84.09; H 5.69; N 4.68
2		285—287 (in sealed capillary)	81.8	N 4.22, 4.41	N 4.28
3		249—250.5	84	N 4.08, 3.62	N 3.89
4		227—228	80.5	N 4.26, 4.02	N 4.28
5		284—285	76.8	N 3.87, 3.61	N 3.70

Found %: N 4.97 (Kjeldahl). $C_{11}H_{12}O_3NBr$. Calculated %: N 4.90.

Upon heating with 30% caustic soda solution, we obtained (III), m.p. 59° [6].

o-Toluidide of benzilic acid (X). 0.3 mole of phenylmagnesium bromide and 0.075 mole (I) were reacted. The organomagnesium complex was decomposed with 10% hydrochloric acid. The ethereal layer was separated and treated with steam. A brown crystalline mass formed in the residue. It was soluble in alcohol, benzene, acetic acid and difficulty soluble in gasoline. It crystallized from alcohol in the form of fine needles. Yield 10.8 g. Constants and analytical data are given in Table 1.

3,3-Diphenyl-7-methyloxindole (V). Concentrated sulfuric acid was run into a solution of 8 g of (X) in 30 ml of glacial acetic acid until there was no brown coloration. The reaction mass was poured into water and the precipitate which formed was treated in the usual manner. Yield 7.3 g. The product was readily soluble in benzene, acetic acid and difficulty – in alcohol. It crystallized from glacial acetic acid in the form of lumps of needles. The constants and analytical data for it are presented in Table 2.

1,1-Diphenyl-3-oxo-5-methyl-3,4-dihydro-2,4-1-benzoxazine (VI). 7 ml of a 50% aqueous solution of chromic anhydride was added to a solution of 7 g of (V) in 30 ml of glacial acetic acid and the reaction mass was heated on a water bath. After the yellow coloration had turned to green, the contents of the flask were poured into 100 ml of water. The precipitate which formed was filtered off, washed with water and dried in air. The yield of product was 2.6 g (35.2%). It dissolved in concentrated sulfuric acid with evolution of carbon dioxide gas and turned a dark red. It was in the form of yellow-brown needles (from alcohol). It melted at 190-192° (with decomp.).

Found %: N 4.36, 4.42. $C_{21}H_{17}O_2N$. Calculated %: N 4.44.

Picrate of 4-methyl-9-phenylacridine (VIII). a) 1 g of (VI) was boiled with 1 ml of nitrobenzene on a sand bath for a period of 1 hour. 10 ml of 10% hydrochloric acid was added and the nitrobenzene was driven off with steam. Upon cooling, the hydrochloric acid solution of the base was filtered free of resinous residue and alkalized with caustic soda solution. The small amount of precipitate which formed was filtered off, dissolved in alcohol and came down in the form of the picrate (VIII) upon addition of an alcoholic solution of picric acid.

b) 5.27 g (0.025 mole) of (IX) and 0.0625 mole of phenylmagnesium bromide were taken for the reaction. The reaction mass was heated for 6 hours on water bath with stirring and it was then decomposed with ammonium chloride solution. The precipitate which formed was treated, upon heating, with 50 ml of 10% hydrochloric acid and was then filtered. Ammonia solution was added to the filtrate until it became basic, and the slight amount of precipitate which formed was filtered off and dissolved in alcohol. An alcoholic solution of picric acid was added to the latter. The picrate precipitated out as the solution stood for two days. A test mixture with the picrate prepared in the previous experiment gave no melting point depression. It was in the form of light yellow plates which melted at 210-211.5°.

Found %: N 11.23, 11.57 (Dumas). $C_{20}H_{15}N \cdot C_6H_2(OH)(NO_2)_3$. Calculated %: N 11.24.

SUMMARY

1. A number of o-toluidides of diarylglycolic acids were synthesized and their properties studied.

2. Under the influence of concentrated sulfuric acid the diarylglycolic acid o-toluidides are transformed in good yields into the 3,3-diaryl derivatives of 7-methyloxindole; here a number of previously unknown compounds were obtained and their properties were studied.

3. The structure of the newly obtained 3,3-diaryl derivatives of 7-methyloxindole was shown on the example of transforming 3,3-diphenyl-7-methyloxindole (V) into 1,1-diphenyl-3-oxo-5-methyl-3,4-dihydro-2,4,1-benzoxazine (VI) and 4-methyl-9-phenylacridine (VIII).

4. It was established that the reaction product of o-toluidine with benzilic acid, having m.p. 278°, was erroneously described by H. Liebig [1] as being 3,3-diphenyl-7-methyloxindole.

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SYNTHESIS AND TRANSFORMATION OF α-GLYCOLS OF THE ETHYLENE SERIES

V. 2-METHYL-3,5-DIPHENYL-4-PENTEN-2,3-DIOL

L. F. Chelpanova, Z. V. Printseva and V. A. Kormer

It is known that α-glycols of the acetylene series under the influence of acid catalysts not only suffer the pinacolin rearrangement, but are also isomerized into unsaturated γ-keto alcohols and substituted hydroxyhydrofurans [1, 2]. It appeared of interest to determine how α-glycols of the ethylene series would behave under these conditions.

In this communication we described the transformations of the cis-isomer of 2-methyl-3,5-diphenyl-4-penten-2,3-diol in the presence of 30% H_2SO_4 and at temperatures of 70 and 100°.

The heating of this ethylene glycol derivative (m.p. 55-56°) with 30% H_2SO_4 at 100° gave acetone, two colorless crystalline substances with m.p. 57-58° (25%) and 135-137° (25%), respectively, and a tarry residue. The colorless crystalline substance with m.p. 57-58° had the empirical formula $C_{15}H_{14}O$ and was characterized as being 1,3-diphenyl-2-propen-1-ol [3].

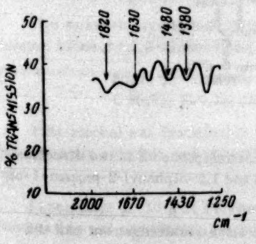

Fig. 1

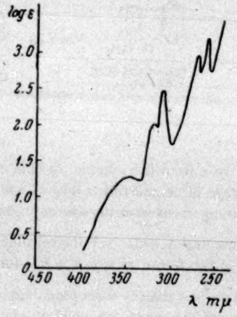

Fig. 2

The substance with m.p. 135-137° had the empirical formula $C_{18}H_{18}O$. The obtained data permitted the assumption that this substance is known 2,4-diphenyl-5,5-dimethyl-2,5-dihydrofuran [4].

Later the experimental conditions for running the reaction were changed: this same α-glycol of the ethylene series was heated at 70° with 30% H_2SO_4. From the acid solution under these conditions were isolated acetone, 1,3-diphenyl-2-propen-1-ol and a yellow crystalline substance with m.p. 98-99° (40%, based on the starting substance). The latter had the empirical formula $C_{18}H_{16}$. The structure of this hydrocarbon was shown by its oxidation with aqueous potassium permanganate solution. The oxidation products, being acetone, benzoic and phthalic acids, permitted assigning to it the formula of 1-isopropylidene-2-phenylindene.

The absorption spectra of this hydrocarbon were studied in the ultraviolet and infrared regions*. An ISP-22 quartz spectrograph was used for photographing the absorption spectra in the ultraviolet region.

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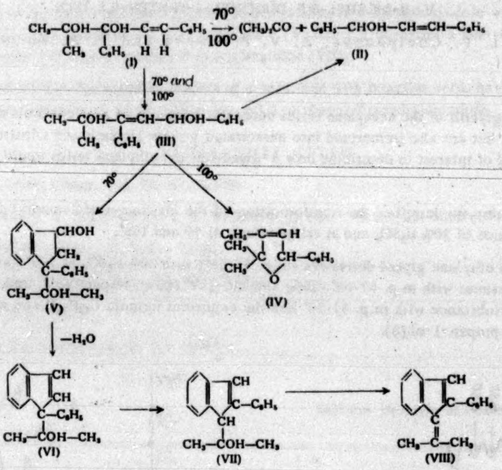
* The authors wish to thank O. N. Setkina for taking the spectra. A hydrogen lamp manufactured by the "Etalon"

The absorption curve of the studied substance in the infrared region (Fig. 1) is characterized by the following fundamental absorption bands: 1480 cm^{-1}, 1630 cm^{-1}, 1380 cm^{-1}, 1820 cm^{-1}, respectively characteristic for the vibrations of the groups $-C=C-$ in the ring, $-CH_3$, and a side-chain double bond, in which connection the 1820 cm^{-1} band determines the presence of a conjugated system of double bonds.

The absorption curve in the ultraviolet (Fig. 2) is characterized by the presence of absorption bands with maxima at 260, 310 and 345 mμ, respectively. The absorption band at 345 mμ shows a similarity to the absorption bands of 2-phenylindene in this region [5].

The formation of the above indicated products at 100 and 70° can be explained by the following scheme:



As can be seen from the scheme, in both cases (at 70 and at 100°) the reaction proceeds in two directions: 1) ketonic cleavage of the starting α-glycol with the formation of acetone [6] and 1,3-diphenyl-2-propen-1-ol; and 2) allyl rearrangement with the hydroxyl jumping into the β-position.

The intermediate γ-(cis- and trans-) ethylene glycol (III) formed in the allylic rearrangement can theoretically exist in two forms, of which one is formed at the higher temperature.

We postulate that the cis-form predominates at 100°, since it is only under these conditions that dehydration with subsequent closure of the dihydrofuran ring to give 2,4-diphenyl-5,5-dimethyl-2,5-dihydrofuran (IV) is possible. The trans-configuration predominates at 70°. Here the formation of the dihydrofuran ring becomes impossible, and the reaction proceeds in the direction of condensation at the double bond with closure of the indene ring (V). Then (V) is dehydrated to (VI) and the hydrogen and phenyl groups change places to give (VII), where the phenyl groups stands in conjugation to the double bond. After this still another molecule of water is cleaved and 1-isopropylidene-2-phenylindene is obtained.

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* plant served as the radiation source for the whole spectrum. The cuvette of variable thickness had a maximum layer thickness of 10 mm. The hexane solutions studied had a concentration ranging from 0.01 to 0.001 mole/liter. The arc spectrum of iron was used to determine the wavelengths in the absorption spectra. The method of equal markings was used in making the photometric measurements.

The above considerations are supported by data found in the literature.

Study of the rearrangement of the unsaturated glycol – 2,5-dimethyl-3-hexen-2,5-diol – revealed that 2,2,5,5-tetramethyl-2,5-dihydrofuran [7] is formed when the cis-isomer of this glycol is treated with 15% H_2SO_4. The trans-isomer under these conditions behaves in a different manner and is 50% converted into the unsaturated hydrocarbon with formula $C_{18}H_{12}$ and m.p. 128°.

EXPERIMENTAL

Experiment 1. 12 g of ethylene α-glycol (m.p. 55-56°) was heated with mechanical stirring in the presence of 30% H_2SO_4 (by weight) at 100° for 3 hours. When heating was completed, the acidic solution was treated with ether. The ethereal extract was washed with 10% soda solution and then with water and was dried with anhydrous sodium sulfate. After the ether was driven off, a yellow-brown syrup remained which then became a dark resin. After repeated treatment of the resin with cold petroleum ether, we isolated 2 g (16%) of a colorless crystalline substance which melted at 135-137°. After separation of these colorless crystals, the resin was treated with hot petroleum ether. After several days, long colorless needles separated out and were easily separated mechanically from the resinous residue. The crystals (1 g, 12%) were recrystallized from petroleum ether, m.p. 57-58°.

After treatment with ether, the aqueous solution gave a positive reaction for acetone. The acetone was driven off from the aqueous solution into a solution of 2,4-dinitrophenylhydrazine. We obtained a 2,4-dintrophenylhydrazone, m.p. 125-126°. A test mixture with the known 2,4-dinitrophenylhydrazone of acetone gave no melting point depression.

The product, colorless crystals, m.p. 135-137°, with difficulty decolorized an aqueous solution of potassium permanganate and bromine water. It gave a negative reaction for the hydroxyl and carbonyl groups.

Found %: C 85.50; H 7.90. M 260. $C_{18}H_{18}O$. Calculated %: C 86.00; H 7.20. M 250.

The compound contained an oxide oxygen and on the basis of analytical data and molecular weight proved to be 2,4-diphenyl-5,5-dimethyldihydrofuran-2,5 [4].

The colorless crystalline substance which melted at 57-58° was shown by analytical data to be the unsaturated alcohol – 1,3-diphenylpropen-2-ol-1 [3].

Found %: C 85.00; H 8.00; OH 8.10. M 216.5. $C_{15}H_{13}(OH)$. Calculated %: C 85.71; H 7.15; OH 8.5. M 210.

This alcohol was described in the literature [3]. For confirmation, the compound was prepared from cinnamic aldehyde and phenylmagnesium bromide. A test mixture gave no melting point depression.

Experiment 2. 10 g of ethylene glycol (m.p. 55-56°) was heated with 30% H_2SO_4 at 70° for 3 hours. After heating was completed, the mixture was treated as described in Experiment 1. The acidic solution was treated with ether; after the ether was driven off, a yellow oil formed which partially crystallized after 0.5 hour of standing. The yellow crystals from the oil were filtered off and recrystallized from alcohol. We obtained 3.0 g (30%) of product; the crystals were lustrous yellow flakes, m.p. 98-99°. After the yellow crystals were separated, the remaining oil was treated with warm petroleum ether. From the petroleum ether we separated crystals, m.p. 57-58°, which proved identical to the above described 1,3-diphenylpropen-2-ol-1 (1.3 g, 13%).

The acidic and neutral solutions, as in the first case, contained acetone. The yellow crystals which melted at 89-99° decolorized an aqueous solution of potassium permanganate and bromine in chloroform and gave a negative reaction for hydroxyl and carbonyl groups.

Found %: C 92.50; H 7.84. M 225. $C_{18}H_{16}$. Calculated %: C 93.10; H 6.89. M 232.

The compound that melted at 98-99° was brominated in the cold in carbon tetrachloride. The bromide was recrystallized from CCl_4 and melted at 126-135° with decomposition.

Found %: C 39.98; H 3.41; Br 57.55. $C_{18}H_{16}Br_4$. Calculated %: C 39.41; H 2.92; Br 57.97.

The bromide was insoluble in benzene and chloroform, soluble in alcohol and carbon tetrachloride.

Oxidation of the yellow compound that melted at 98-99° was performed under the following conditions: 1.5 g of the compound was placed in a flask fitted with mechanical stirrer, 50 ml of 2% $KMnO_4$ was added and then at 30-50° in the course of 3 days, 1.5 g of potassium permanganate was added in small portions to the reaction mixture. After the reaction was complete, the initial compound could not be detected among the neutral products. Upon acidification of the organic acid salts and after the reaction mixture had stood for 5 days, 0.4 g of crystals came down which melted at about 200° with decomposition. The presence of phthalic acid was confirmed by a fluorescein test [8]. Besides this, phthalimide, m.p. 235-237° was obtained; a test mixture with known phthalimide gave no melting point depression. Steam distillation of the aqueous solution yielded benzoic acid which was isolated in its pure state by sublimation; m.p. 119-120°. We prepared its silver salt.

Found %: Ag 42.79. $C_7H_5O_2Ag$. Calculated %: Ag 41.99.

Acetone was detected in the aqueous solution and gave the 2,4-dinitrophenylhydrazone, m.p. 125-126°.

SUMMARY

1. The treatment of 2-methyl-3,5-diphenyl-4-penten-2,3-diol with 30% sulfuric acid at 100° leads to allylic rearrangement with the formation of 2,4-diphenyl-5,5-dimethyl-2,5-dihydrofuran and simultaneous ketonic cleavage with the formation of acetone and 1,3-diphenyl-2-propen-1-ol.

2. The treatment of 2-methyl-3,5-diphenyl-4-penten-2,3-diol with 30% sulfuric acid gives mainly the previously unknown 1-isopropylidene-2-phenylindene, and also 1,3-diphenyl-2-propen-1-ol and acetone.

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THE PREPARATION OF ARYLHALOMONOSILANES

E. M. Soshestvenskaya

Together with other secondary products, tetraalkyl- or tetraarylmonosilanes [1] are obtained in the synthesis of alkyl- and arylhalomonosilanes by the reaction of halogen-substituted hydrocarbon derivatives with a silicon-copper melt. The former can also be obtained without any great difficulty in a different manner, for example, by the reaction of mixed organomagnesium compounds with the salts of hydrofluorosilicic acid [2]. In connection with this it appeared of interest to find the conditions for the transformation of the tetraalkyl- and tetraarylmonosilanes into the alkyl- or arylhalomonosilanes – valuable substances in the applied sense, realizing such transformations without losing a portion of the organic radicals of the organosilicon compound as the result of transition into organometallic compounds [3], or in the formation of hydrocarbons [4] or halogen-substituted hydrocarbon derivatives [5].

Based on the data given in the studies of Sauer and Hadsell [6], showing that trimethylchloromonosilane at 375° and with participation of catalysts of the type of $AlCl_3$, $ZnCl_2$, $FeCl_3$, CuCl and $BiCl_3$ suffers rearrangement into an equilibrium mixture, composed of 6.9% tetramethylmonosilane, 80.8% trimethylchloromonosilane and 12.3% dimethyldichloromonosilane, it could be expected that tetraphenylmonosilane, containing phenyl groups that are replaced with comparative ease by halogen atoms, will react with silicon tetrachloride to give arylhalomonosilanes and, in particular, triphenylchloromonosilane.

Since $AlCl_3$ reacts with tetraphenylmonosilane to give $C_6H_5AlCl_2$ and the diphenyldichloromonosilane and triphenylchloromonosilane enter into a similar reaction [7], then as catalyst we used cuprous chloride. As the end result of heating a mixture of tetraphenylmonosilane and silicon tetrachloride with this catalyst for 12 hours at 300-360° we obtained the triphenylchloromonosilane in 34% yield, which was isolated by converting it into the triphenylsilicol.

EXPERIMENTAL

A mixture of 16.5 g tetraphenylmonosilane, 25 g silicon tetrachloride and 1 g cuprous chloride was heated in five sealed tubes at 300-360° for 12 hours. After the reaction product, which remained liquid on cooling, had been separated from the precipitate of cuprous chloride, it was fractionated. The 1st fraction (15.15 g), which distilled over in the interval 60-65°, consisted of silicon tetrachloride; the 2nd (3.92 g) distilled over at 66-111° and the 3rd (3.19 g) – at 111-345°. The residue from the distillation weighed 15.34 g. The 2nd and 3rd fractions contained phenylchloromonosilanes. The residue from distillation was hydrolyzed. Repeated fractional recrystallizations of the hydrolysis product from benzene yielded 8.34 g of initial tetraphenylmonosilane and 4.15 g of triphenylsilicol, m.p. 153-155°. Subsequent recrystallization yielded a product that melted at 154-155°.

Found %: C 78.15; H 5.87; Si 10.07. $C_{18}H_{16}OSi$. Calculated %: C 78.21; H 5.84; Si 10.17.

When a similar experiment was performed in the temperature range 250-300°, after hydrolysis of the reaction product we isolated only a slight amount of triphenylsilicol and almost all the initial tetraphenylmonosilane.

SUMMARY

It was established that tetraphenylmonosilane is capable of reacting with silicon tetrachloride in the presence of cuprous chloride to give triphenylchloromonosilane in about 34% yield.

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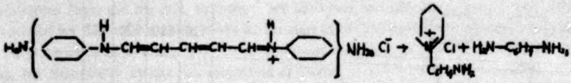
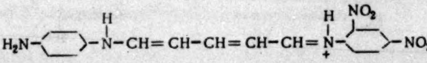
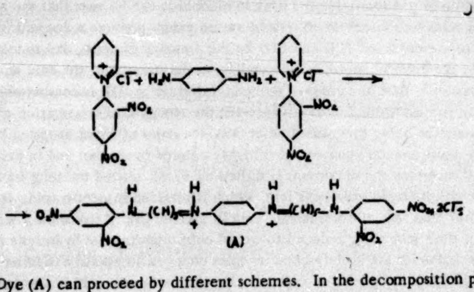
THE REACTION PRODUCTS OF 2,4-DINITROPHENYLPYRIDINIUM CHLORIDE WITH DIAMINES

N. E. Grigoryeva and I. K. Gintse

Depending on the medium and the structure of the diamine, in the condensation of 2,4-dinitrophenylpyridinium chloride with diamines the starting substances can react in different proportions. The diamines with one substituted amino group react with the starting quaternary salt by the usual scheme [1] to give symmetrical amino-substituted pyridine dyes. The unsubstituted phenylenediamines (o-, m- and p-) react by a similar scheme when their condensation with dinitrophenylpyridinium salts is run in alcohol for a short time. Together with the amino-substituted derivatives, prolonged heating of the diamine (o- or p-) with the original salt gives an unsymmetrical pyridine dye (for the o-isomer) and a bis-pentamethine dye (for the para-isomer). In their properties the amino-substituted dyes differ sharply from the unsymmetrical dye, and also from the bis-pentamethine. The structure of the latter can be represented on the basis of their synthesis and a study of their decomposition products. When the symmetrical amino-substituted dyes (meta-isomers) were decomposed, which proceeds in known manner [2], they gave the corresponding aminophenylpyridinium chlorides.

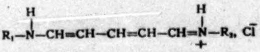
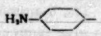
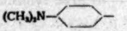
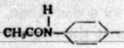
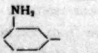
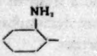
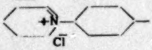
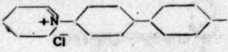
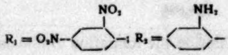
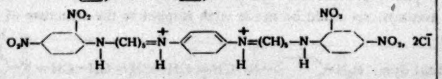


When the condensation was run with p-phenylenediamine hydrochloride the formation of dinitroaniline could not be shown, and consequently two assumptions could be made with respect to the structure of the dye obtained here. It could be the unsymmetrical dye:  $H_2N-C_6H_4-\overset{H}{N}-CH=CH-CH=CH-CH=\underset{+}{\overset{H}{N}}-C_6H_3(NO_2)-NO_2, \bar{Cl}$, the decomposition of which could result in the cleavage of dinitroaniline and the formation of p-aminophenylpyridinium chloride. However, its behavior toward acids and alkalies, and also the analysis data, refute such a postulation. Without removal of dinitroaniline the bis-pentamethine dye could be formed, provided one molecule of the diamine reacts with two molecules of the original salt:



The decomposition of Dye (A) can proceed by different schemes. In the decomposition products we found dinitroaniline, p-aminophenylpyridinium chloride and a water-soluble dye of unknown structure. However, it must be kept in mind that in the thermal decomposition, and also in the decomposition of the dye in pyridine, the resulting products can react between themselves in a different manner; in addition, a small amount of tarry products is always obtained here, which greatly complicates elucidation of the cyclization mechanism for the dye. The formation of a considerable amount of dinitroaniline and p-aminophenylpyridinium chloride makes the second postulation highly probable.

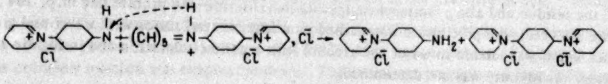
The spectrophotometric measurement results for 9 of the studied dyes are given in the table.

Dye No.	 $R_1-\overset{H}{N}-CH=CH-CH=CH-CH=\underset{+}{\overset{H}{N}}-R_2,\ Cl^-$	λmax. (in mμ)				
		C_2H_5OH	C_2H_5OH + HCl	CH_3COOH	HCOOH	C_2H_5OH + NaOH
	$R_1 = R_2$					
I		530	493	495	483	—
II		550	495	495	475	—
III		508	508	500	497	—
IV		500	495	495	495	—
V		450	450	495	450	—
VI		507	507	507	503	—
VII		510	510	520	517	—
VIII•		—	—	—	—	525
IX		565	563	—	600	—

• The dye was obtained as the free base.

From a comparison of the absorption maxima in alcohol it can be seen that the amino-substituted pyridine dyes obey the general rules for color — the alkylated amino groups produce a deepening, and the acylated amino groups a heightening of the color (cf. I, II and III). In the presence of acids, due to salt-formation and "insertion" of auxochrome groups, the color is raised, but depending on the strength of the acid and the "basicity" of the cation this effect is variable; thus, the color of the acetyl derivative (III) is considerably higher only in formic acid. For all of the amino-substituted derivatives (I-III) the strongest salt-formation of the amino groups proceeds in formic acid, an exception being the meta-isomer (IV), the color of which is raised but slightly in all acids. The ortho-isomer (V) shows unusual behavior, it is highly colored in alcohol and in acid solutions, with the exception of acetic acid, in which the maximum is shifted by 45 mμ toward the long wavelengths. Its high color is possibly associated with its rapid hydrolysis rate, which is retarded in acetic acid. It is known that the acidity of acetic acid is greater than that of hydrochloric acid in alcohol [3]. Acids show a weak influence on the color of dyes (VI) and (VII), their role being reduced to one of only retarding the hydrolysis reaction. Dye (VIII) shows weak basic properties and acids fail to influence its color changes, in alkaline medium it is transformed into a colored anion. The profound deepening of color for Dye (IX) in formic acid is also probably associated with hydrolysis inhibition.

As was already mentioned above, a study of the decomposition permits establishing the structure of the dyes; however, it was not only from this viewpoint that the cyclization reaction was of interest to us. All of the dyes studied by us were subjected to cyclization for the purpose of studying the reaction itself and the N-arylpyridinium salts that are formed here. The aminophenylpyridinium chloride derivatives with substituted amino groups were isolated with comparative ease, while the unsubstituted derivatives, especially the m-isomer, were isolated with difficulty, since they probably form addition products [4] with the phenylenediamines, which are hydrolyzed with difficulty. The o-aminophenylpyridinium chloride was not obtained. p-Aminophenylpyridinium chloride, similar to amines with other electron-acceptor groups, reacts with the starting quaternary salt only in the presence of pyridine [5]. The dipyridinium dye formed under these conditions is easily cyclized into p,p'-phenylenedipyridinium chloride:



The aminophenylpyridinium chlorides fail to be cleaved by alkali in the cold, but when heated they form the monoanilides of glutaconic aldehyde. In alcohol solution the hydrochlorides of the aminophenylpyridinium chlorides, in which the stabilizing influence of the NH_2 group on the $-C=N$ bond of the pyridine ring is neutralized, are cleaved by alkali in the cold.

By heating our earlier obtained cyclization product of the benzidine derivative of glutaconic aldehyde [6] with hydrochloric acid and subsequent neutralization with ammonia we obtained p-aminophenylpyridinium chloride, which with the starting quaternary salt gives the dipyridinium dye (VII).

EXPERIMENTAL •

It is known that pyridine dyes crystallize together with the solvent. After complete removal of solvent, the dyes absorb moisture from the air and, therefore, we analyzed the air-dried compounds. The amount of solvent was determined by drying the compounds in vacuum (120-130 mm) over phosphorus pentoxide at the boiling point of ethyl alcohol or xylene. The determinations for nitrogen were performed according to the micromethod of Dumas, for chlorine – by the micromethod of Carius.

Chloride of 4,5-bis-(p-phenylenediamino)-pentadien-1,3-ylidene-5. A hot solution of 5.2 g 2,4-dinitrophenylpyridinium chloride in 10 ml of alcohol was run into a solution of 4 g of freshly prepared p-phenylenediamine in 5 ml of alcohol; a dark precipitate immediately formed. The mixture was heated on a boiling water bath for 10 minutes. The dye was washed on a filter with water and then with acetone until there was no red coloration when alkali was added to the acetone solution. We isolated 4.6 g of dye (76%) in the form of dark crystals, soluble in alcohol with a red-violet color. We could not recrystallize the dye. It was purified by repeated washing with warm acetone, water, alcohol and ether; it melted at 167°. It contained solvent.

Found %: N 16.24, 16.39. $C_{17}H_{19}N_4Cl \cdot {}^1/_2\ C_2H_5OH$. Calculated %: N 16.59.

p-Aminophenylpyridinium chloride 14.42 g of dye was heated in a drying oven at 128-133° and a colorless substance (p-phenylenediamine) sublimed off. The dye partially fused and turned dark brown. The amine was removed with repeated washings, upon heating the product with acetone. We isolated 10 g of light brown substance which was dissolved in ethyl alcohol and precipitated with a large excess of ether; it was in the form of fine yellow crystals, yield 6.1 g (60%). After two recrystallizations from anhydrous alcohol, it was in the form of dense brown crystals, m.p. 252°. Diazotization revealed the presence of one amino group. The loss in weight after drying was 8.87% which corresponded to $^1/_2$ molecule of ethyl alcohol.

Found %: N 12.32, 12.29; Cl 15.46, 15.28. $C_{11}H_{11}N_2Cl \cdot {}^1/_2\ C_2H_5OH$. Calculated %: N 12.20; Cl 15.47.

Picrate of p-amino-phenyl pyridine was recrystallized twice from water and alcohol; it was in the form of yellow crystals, m.p. 164°.

Found %: N 17.55, 17.61. $C_{17}H_{19}O_7N_5$. Calculated %: N 17.54.

• S. F. Rybkina participated in the experimental work.

Chloride of 5,1'-(p-phenylenediamine)-1,5'-bis-(2,4-dinitroaniline)-pentadien-1,3,1',3'-ylidene-5,5'. A mixture of 1.3 g of p-phenylenediamine hydrochloride, 1 g of 2,4-dinitrophenylpyridinium chloride in 5 ml of alcohol and 2 ml of pyridine was heated on a boiling water bath for 15 minutes. At first, after the precipitate came down, the violet color of the mixture turned to red. The precipitate was washed on a filter with water, acetone and ether. We obtained 0.9 g of a mixture of dyes which was resolved by chromatography on aluminum oxide. We isolated a symmetrical amino derivative (1) and green crystals, difficultly soluble in alcohol, m.p. 240°. The dye was readily soluble in formic acid and water, less soluble in acetic acid from which it was recrystallized. It contained solvent.

Found %: N 14.96, 15.03. $C_{28}H_{24}O_8N_8Cl_2 \cdot CH_3COOH$. Calculated %: N 15.32.

Decomposition of dye. 1 g dye in 10 ml pyridine was heated on a wire gauze with reflux condenser for 1 hour. The brown solution was filtered off and steamed down over a water bath. Dinitroaniline (extracted with acetone) was detected in the residue and also p-aminophenylpyridinium chloride— the picrate had m.p. 164°. After decomposition of the dye-stuff, the precipitate was washed on a filter several times with water and yielded a green crystalline product which was soluble in water and alcohol with a yellow coloration and in formic acid with a red-violet coloration. Its identity was not determined.

After thermal decomposition of the dye (at 220°), the melt was treated with acetone, the dinitroaniline was extracted, the residue was dissolved in water and the picrate was obtained in the form of yellow crystals which melted at 163-164°. Thus, after decomposition of the bis-pentamethine dye (IX), we isolated dinitroaniline, p-aminophenylpyridinium chloride and a small quantity of dye whose structure was not determined.

Chloride of 1,5-bis-(acetyl-p-phenylenediamine)-pentadien-1,3-ylidene-5. Condensation of the initial quaternary salt with acetyl-p-phenylenediamine in alcohol yielded the dye-stuff in the form of fine violet crystals, yield 55%. After recrystallization from acetic acid, the product was in the form of violet crystals, m.p. 147°. It contained traces of solvent.

Found %: N 13.75, 13.83. $C_{21}H_{23}O_2N_4Cl$. Calculated %: N 14.05.

P-Acetylaminophenylpyridinium chloride. 1 g of dye was heated in a drying oven until it melted. The fusion was treated with water, decolorized with carbon, steamed down, and after being washed with acetone was in the form of a powder with a slight pinkish tinge. Upon purification of the salt by precipitation from decolorized alcohol solution with ether, it was in the form of clumps of small needles which slightly darkened in air, m.p. 276-277°. Heating with caustic soda caused cleavage.

Found %: N 11.34, 11.34; Cl 14.25, 14.10. $C_{13}H_{13}ON_2Cl$. Calculated %: N 11.27; Cl 14.29.

The picrate was in the form of yellow crystals, m.p. 189°.

Chloride of 1,5-bis-(p-aminodimethylaniline)-pentadien-1,3-ylidene-5 was obtained, yield 57%, in the form of violet crystals (from alcohol), m.p. 147°. It contained traces of solvent.

Found %: N 14.88, 14.95. $C_{21}H_{27}N_4Cl$. Calculated %: N 15.13.

p-Dimethylaminophenylpyridinium chloride was prepared by decomposition of the dye in water. The treatment was the same as for p-aminophenylpyridinium chloride. After recrystallization from a mixture of acetone and ethyl alcohol (6:1), we isolated the quaternary salt, yield 53%, in the form of golden-yellow needles, m.p. 114°; it contained solvent. The loss in weight after drying was 16% which corresponded to 1 molecule of alcohol.

Found %: N 9.94, 9.99. $C_{13}H_{15}N_2Cl \cdot C_2H_5OH$. Calculated %: N 9.98.

1-(p-Aminodimethylaniline)-pentadien-1,3-al-5. When a concentrated aqueous solution of the hydrochloride of p-dimethylaminophenylpyridinium chloride was heated with a 20% caustic soda solution, we obtained lustrous green crystals (orange under the microscope) from the red solution. The product, washed several times with water and ether, melted at 240° (with decomp.). It was soluble in dichloroethane, absorption maximum — 535 mμ, in acetone — 480 mμ and in alcohol — 470 mμ. Its yield was 69% (based on the salt).

Found %: N 13.22, 13.04. $C_{13}H_{16}ON_2$. Calculated %: N 12.96.

p-p'-Phenylenedipyridinium chloride. A mixture of 1 g of 2,4-dinitrophenylpyridinium chloride and 1.6 g of p-aminophenylpyridinium chloride in 10 ml of ethyl alcohol was heated for 5 minutes on a water bath. About 1 ml of pyridine was added to the hot brown solution and an intense red coloration immediately appeared.

Heating of the mixture was continued until a negative reaction was obtained in testing for the presence of 2,4-dinitrophenylpyridinium chloride. After two hours of heating, upon cooling, the dark precipitate which came down was filtered off (dinitroaniline) and the filtrate was evaporated to dryness over a water bath. The dry residue was heated several times with acetone to remove traces of dinitroaniline and then was dissolved, upon heating, in 10 ml of ethyl alcohol, filtered, and precipitated with an excess of acetone. We obtained 0.9 g of an orange-red compound, soluble in alcohol with a yellow coloration and a strong green fluorescence; upon addition of hydrochloric acid, the color went to orange-red (507 mμ). This compound was the dipyridinium salt, stained by the dye. After decolorization with carbon, the salt was precipitated from alcoholic solution with acetone. We obtained 0.65 g of pale-yellow crystalline substance, readily soluble in water and alcohol. It did not melt and carbonized upon heating. The action of alkali upon its aqueous solution produced an intense yellow coloration. The action of aqueous alkali upon the dry salt yielded a brown substance, soluble in acetone with an orange coloration, in alcohol – yellow, and in alcohol in the presence of acid – orange-red.

The dipyridine salt was purified through the double mercuric salt which was recrystallized from water in the form of faint-yellow lustrous flakelets, m.p. 285°. After decomposition of the mercuric salt with hydrogen sulfide, the colorless solution was evaporated down. The salt was reprecipitated from anhydrous alcohol with ether. It contained solvent. The loss in weight after drying was 15.58%, corresponding to $1^1/_4$ molecules of alcohol.

Found %: N 7.54, 7.69; Cl 19.72, 19.32. $C_{16}H_{14}N_2Cl_2 \cdot 1^1/_4\, C_2H_5OH$. Calculated %: N 7.72; Cl 19.59.

The picrate, recrystallized from water, was in the form of lemon-yellow crystals, m.p. 233°.

Found %: N 15.99, 16.20. $C_{28}H_{18}O_{14}N_8$. Calculated %: N 16.23.

Chloride of 1,5-bis-(m-phenylenediamino)-pentadien-1,3-ylidene-5. A solution of 18 g of m-phenylenediamine in 20 ml of ethyl alcohol was added to a hot solution of 23 g 2,4-dinitrophenylpyridinium chloride in 40 ml of alcohol. The mixture was heated for 30 minutes. After purification by washing (with water, alcohol and acetone), we obtained 19 g of dye in the form of greenish-brown powder, difficultly soluble in water and soluble in alcohol with an orange-red coloration. On reprecipitation from alcohol, it was in the form of a dark-red finely crystallized powder, m.p. 198-200°. It contained solvent.

Found %: N 13.71, 13.84. $C_{17}H_{19}N_4Cl \cdot 2C_2H_5OH$. Calculated %: N 13.78.

m-Aminophenylpyridinium chloride. 1 g of dye was heated in a drying oven to 182°; the crystals on top slightly fused. This fusion, on being rubbed, was in the form of a dark brown powder, soluble in water and alcohol with a yellow-brown coloration and a strong green fluorescence. Upon addition of acid, the color did not change but the fluorescence intensified. Upon heating, the product dissolved in alcohol and was passed through a column containing aluminum oxide and an excess of ether was added to the brown solution until a precipitate came down. We isolated a dark brown product, m.p. 258°. It contained solvent. The alcoholic solution was yellow with green fluorescence. We found 13.63% nitrogen, corresponding to a compound containing 2 molecules of aminophenylpyridinium chloride with 1 molecule of phenylenediamine and 2 molecules of alcohol. After separation, ether was again added to the mother liquor and the mixture was set aside for a day. Long yellow needles, readily soluble in water, came down, m.p. 75°. Upon reprecipitation from alcohol with ether, the product gave pale yellow needles, m.p. 78°. It was readily soluble in acid and after concentration, the colorless precipitate gave a yellow coloration with alkali and after heating – a red one. It contained solvent. The loss in weight after drying was 9.5%, corresponding to $^1/_2$ molecule of alcohol.

Found %: N 12.30, 12.16. $C_{11}H_{11}N_2Cl \cdot {}^1/_2\, C_2H_5OH$. Calculated %: N 12.20.

Chloride of 1,5-bis-(o-phenylenediamine)-pentadien-1,3-ylidene-5. 1 g o-phenylenediamine was added to a hot solution of 1.2 g initial salt in 10 ml of alcohol. The thick red solution was heated to the boil for 3 minutes and left standing overnight. The dark, almost black crystals were washed with acetone, water, alcohol and ether. We isolated 0.2 g of finely crystalline precipitate, soluble in alcohol, with an orange-red coloration and in pyridine – bright red; m.p. 160°.

Found %: N 16.36. $C_{17}H_{19}N_4Cl \cdot {}^1/_2\, C_2H_5OH$. Calculated %: N 16.59.

A dye in the form of a resin was precipitated from the mother liquor with ether; it was readily soluble in alcohol giving a fuchsine, and in acetone, a blue-violet coloration; we could not isolate the product in a crystalline state.

1-(2,4-Dinitroaniline)-5-(o-phenylenediamine)-pentadien-1,3-ylidene-5. A mixture of 3 g of o-phenylenediamine and 3.8 g of 2,4-dinitrophenylpyridinium chloride in 20 ml of alcohol was heated for 20 minutes. Brown crystals separated out of the hot solution and were filtered off and washed the next day; after recrystallization from pyridine, they had m.p. 225°. We isolated 0.3 g of compound which was difficultly soluble in alcohol, giving yellow coloration; in the presence of acid the color did not change, alkali deepened the color, in alcohol it was fuchsine and in acetone – violet.

Found %: N 18.46, 18.48. $C_{17}H_{16}O_4N_5Cl$. Calculated %: N 17.81.

The compound was again analyzed after standing for 2 days.

Found %: N 18.95; Cl 2.20, 2.15. $C_{17}H_{16}O_4N_5Cl$. Calculated %: N 17.81; Cl 9.11.

The compound was dissolved in pyridine and precipitated with water, washed on a filter several times with water and did not contain chlorine. It was readily soluble in acetone giving an orange coloration and upon addition of alkali, the color turned blue-violet. It contained solvent.

Found %: N 18.41. $C_{17}H_{15}O_4N_5 \cdot 1^1/_2 H_2O$. Calculated %: N 18.42.

After the compound was thermally decomposed, dinitroaniline separated out and the resinified product was probably o-phenylenediamine.

p-Aminodiphenylpyridinium chloride. 3.4 g of yellow substance – the product of decomposition of the benzidine derivative of glutaconic aldehyde [4] – was dissolved, upon heating, in concentrated hydrochloric acid. After cooling the solution was carefully neutralized with ammonia and an orange-yellow crystalline product came down which was readily soluble in water and alcohol, difficultly soluble in acetone; it recrystallized from ethyl alcohol in the form of yellow flakes, m.p. 307°. Yield 1.2 g. Diazotization revealed the presence of one amino group. The product was dried in vacuum.

Found %: N 9.93, 9.88; Cl 12.51, 12.44. $C_{17}H_{15}N_2Cl$. Calculated %: N 9.91; Cl 12.57.

Chloride of 1,4-bis-(p-aminodiphenylpyridinium chloride)pentadien-1,3-yliden-5. A mixture of 0.5 g of p-aminodiphenylpyridinium chloride and 0.5 g 2,4-dinitrophenylpyridinium chloride in 10 ml of alcohol was heated with 2 ml of pyridine on a water bath for 15 minutes and set aside for 12 hours. After being washed on a filter, the red precipitate was reprecipitated from alcohol with hydrochloric acid; it weighed 0.4 g (57%). The dye decomposed without fusion. It contained solvent. The loss in weight after drying was 17%, corresponding to 3 molecules of alcohol.

Found %: N 6.97, 7.06; Cl 13.19, 13.35. $C_{39}H_{33}N_4Cl_3 \cdot 3C_2H_5OH$. Calculated %: N 6.99; Cl 13.29.

SUMMARY

1. Nine pyridine dyes were obtained by the reaction of 2,4-dinitrophenylpyridinium chloride with diamines and their properties were studied.

2. Depending on the condensation conditions, it was established that the diamines with unsubstituted amino groups can react with the starting pyridinium salt in the ratios: 2:1, 1:1 and 1:2.

3. The cyclization of the studied dyes gave 6 new N-arylpyridinium salts.

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THE SYNTHESIS OF A NUMBER OF DERIVATIVES BASED ON 2,4-DICHLORO-2-BUTENE

SYNTHESIS AND PROPERTIES OF 2-CHLORO-4-MERCAPTO-2-BUTENE

A. L. Klebansky and G. T. Essayan

2,4-Dichloro-2-butene is characterized by a high reactivity of the allylic chlorine. In this communication we describe the reaction of 2,4-dichloro-2-butene with sodium hydrosulfide to give the mercaptan (I). This compound can be of interest both in itself and for further syntheses. In alcohol medium a product was isolated that failed to show the characteristic reactions of mercaptans. This product can be assumed to be 2-chloro-4-ethoxy-2-butene (II), formed in the reaction of 2,4-dichloro-2-butene with ethyl alcohol in the presence of alkali. Under our conditions the latter is formed as the result of the partial hydrolysis of either NaSH or Na_2S [1]. Together with the solvent, the concentration of the sodium hydroxide in the aqueous hydrosulfide solution also has an important bearing on the formation of the mercaptan.

As is known from the literature [2], mercaptans, in the presence of alkalies, react with alkyl chlorides, being transformed into the corresponding sulfides. In the case of 2,4-dichloro-2-butene the formation of compound (III) can be expected:

$CH_3-CCl=CH-CH_2SH$ (I)

$CH_3-CCl=CH-CH_2-OC_2H_5$ (II)

$CH_3-CCl=CH-CH_2-S-CH_2-CH=CCl-CH_3$. (III)

This compound was not isolated by us; however, when NaSH solution with a high NaOH content was used we observed a sharp reduction in the mercaptan yield and the formation of secondary, higher-boiling products, which were not investigated.

The 2-chloro-4-mercapto-2-butene (I) obtained by us has a sharp, disagreeable odor, characteristic for mercaptans. On prolonged exposure to the air it slowly oxidizes to the disulfide. In the complete absence of air, or when its admittance is limited, and in the absence of light it can be kept for quite some time (3-4 months) without significant changes. Its reaction with iodine also gives the disulfide. The latter reaction is used for the quantitative determination of mercaptans [3]. However, when the iodometric method is used for the quantitative determination of 2-chloro-4-mercapto-2-butene there is some abnormal consumption of iodine. This can be explained by the presence of a double bond, which shows partial addition of iodine in this case. The product obtained in the reaction with iodine, namely the disulfide, was not individualized.

Attempts to improve the iodometric determination results by using solvents and by running the titration in solutions also gave unfavorable results. It was experimentally shown that under these conditions the 2-chloro-4-mercapto-2-butene is oxidized very slowly, which is not feasible in practice. Like all mercaptans [4], 2-chloro-4-mercapto-2-butene (I) gives the silver, mercury and lead mercaptides. The latter suffer decomposition without melting. The mercaptan is soluble in both alkali and in ammonia, the former being the better solvent. Dissolving the mercaptan in alkali can serve as a method for its separation from the sulfide, the starting dichloride and other reaction impurities.

EXPERIMENTAL

Preparation of 2-chloro-4-mercapto-2-butene(I) by the reaction of 2,4-dichloro-2-butene with an aqueous solution of NaSH. 56.3 g 2,4-dichloro-2-butene and 350 ml aqueous NaSH solution, prepared by passing H_2S through an aqueous solution of NaOH (the NaSH content was 94 g/liter), were placed in a flask fitted with stirrer and reflux condenser. The reaction mixture, with continuous stirring, was heated on a boiling water bath for 6 hours; after this, the oily layer was separated off and agitated with a 25% aqueous solution of NaOH; at this point the mercaptan dissolved but the admixtures (initial dichloride, sulfide and disulfide) remained unchanged. After the admixtures were separated off, the alkaline solution of the sodium mercaptide was acidified with hydrochloric acid; the mercaptan which separated out was washed with water and dried over Na_2SO_4. Upon vacuum-distillation, we collected the fraction that boiled at 68-68.5° at 50 mm. Yield 55%.

d_4^{20} 1.1232, n_D^{20} 1.5102, MR_D 32.63; calc. 32.76.

Found %: Cl 29.1; S 26.02. C_4H_7ClS. Calculated %: Cl 28.98; S 26.11.

When NaSH solutions containing 15 to 25 g/liter of NaOH were used, the yield was sharply reduced. The boiling points of the mercaptan at various pressures are given in Table 1.

TABLE 1

Pressure (in mm)	Boiling point
50	68-68.5°
100	85-86
150	92-93
200	99-100
300	107-108
500	123-124
680	145 (with decomp.)

TABLE 2

Content of mercaptan in improvised mixture (in %)	Content for mercaptan (in % with respect to initial mixture)	
	by I	by HI
60	103.3	94.3
	106.6	92.8
70	103.8	98.4
80	95.9	98.0
85	104.1	96.7
	104.0	94.0

Study of the reaction of the mercaptan with iodine. (Experiments of quantitative determination of the mercaptan in commercial mixtures). Experimental studies of the reaction of the mercaptan with iodine were made to determine the possibility of quantitative determination of the mercaptan in commercial mixtures. The reaction was performed with an iodine solution in various media — aqueous, alcoholic and benzene.

Experiments in aqueous medium. A weighed portion of the mercaptan, 0.1-0.15 g, was placed in a Zhukov flask (shielded from light) which contained 50 ml of 0.025 N iodine solution, and the contents of the flask were stirred for 1 hour. The excess of iodine was titrated with 0.025 N $Na_2S_2O_3$ solution. Calculation was on the basis of the following equation for the reaction:

$$2CH_3CCl{=}CHCH_2SH + I_2 \longrightarrow 2HI + CH_3CCl{=}CHCH_2{-}S{-}S{-}CH_2CH{=}CClCH_3.$$

In view of the possibility that the iodine might be partially consumed as the result of addition to the double bond of the mercaptan itself and to that of the possibly admixed dichloride (without considering a substitution reaction which is less probable under the conditions cited) we also determined the amount of HI that separated out during the reaction. For this purpose, after combination of the excess iodine with hyposulfite, the HI was titrated with 0.025 N NaOH solution in the presence of methyl red as an indicator. The analytical results on improvised mixtures are given in Table 2.

The data of Table 2 show that the iodometric method gave rather high results of the iodine consumed and low results by HI in the range of 3-7% of the absolute values. In order to secure a more uniform distribution of the mercaptan in the solution during titration, analyses were performed with alcohol and benzene as solvents. These experiments showed that the reaction of the mercaptan with iodine in these solvents goes very slowly and is not complete (Table 3).

Reaction of the mercaptan with alkali. To determine the solubility of the mercaptan in solutions of NaOH of various concentrations we took a measured volume of the mercaptan in a 100 ml test tube with 0.1 ml divisions and, upon shaking, added alkali in varied amounts to secure various concentrations and excesses of the latter in the solution. It was determined that the maximum solubility in alkali (about 85-87% of the quantity of the mercaptan present) was attained for the commercial product with an 87.4% mercaptan content when 20-25% alkali was used in 50% excess. The solubility of the mercaptan in the alkaline solutions decreased with increase of dilution with foreign substances such as benzene, ether or initial 2,4-dichloro-2-butene.

TABLE 3

Solvent	Content of mercaptan (in %)			
	5 minutes	1 hour	1.5 hour	18 hours
Alcohol	54.4	67.9	66.4	–
	61.8	–	–	68.1
	2 hours	4 hours	24 hours	–
Benzene	73.2	70.7	77.8	–

Preparation of mercaptides of heavy metals. Silver mercaptide. 25 ml 0.1 N $AgNO_3$ solution was added to a solution of 0.5 g of mercaptan (I) in 20 ml ethyl alcohol and the mixture was heated on a water bath. A white precipitate formed which after filtration and drying at room temperature, gradually darkened in air. The precipitate was insoluble in alcohol and decomposed at 158° without melting.

Mercury mercaptide. An excess of mercuric oxide was added to a solution of the mercaptan in ethyl alcohol. The mixture was heated on a water bath with reflux condenser for a half hour and then filtered while hot. Needles, m.p. 80-81° (after recrystallization from alcohol) came down from the filtrate.

Found %: Cl 16.59, 16.93; S 15.58, 15.57. $C_8H_{12}S_2Cl_2Hg$. Calculated %: Cl 16.01; S 14.43.

The reaction of a solution of the mercaptan with mercuric cyanide yielded a mercury derivative of a different composition and structure. 20 ml of a 10% solution of $Hg(CN)_2$ was added to a solution of 0.5 g of mercaptan (I) in 20 ml alcohol and the mixture was heated on a water bath. A white flaky precipitate formed which was filtered off, washed with water, and dried at room temperature. The isolated mercury compound was difficultly soluble in ethyl alcohol. It decomposed at 248° without melting. This compound was not analyzed further.

Lead mercaptide. 45 ml of 20% lead acetate solution was added to a solution of 3 g of mercaptan in 20 ml ethyl alcohol. The mixture was heated on a water bath and formed a yellow amorphous mass upon cooling.

Copper mercaptide. A solution of equal quantities of copper sulfate and sodium acetate was added to the mercaptan. A yellowish amorphous precipitate came down. After being washed with water and ether, the product was analyzed for chlorine content according to Carius.

Found %: Cl 20.24, 20.24. C_4H_6ClSCu. Calculated %: Cl 19.19.

The isolated mercaptide of copper was unstable; upon standing it gradually darkened and decomposed without melting when it was heated above 100°. It was virtually insoluble in ordinary solvents.

SUMMARY

1. The mercaptan $CH_3-CCl=CH-CH_2SH$ was obtained by the reaction of 2,4-dichloro-2-butene with sodium hydrosulfide.

2. The reactions of the mercaptan were studied and a number of its derivatives were prepared.

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NAPHTHOFUROXAN

IV. DERIVATIVES OF 1,2-NAPHTHOQUINONE-6-SULFONIC ACID DIOXIME

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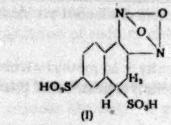
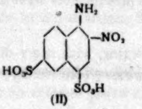
As was mentioned earlier [1], the oxidation of the bisulfite compound of 1,2-naphthoquinone dioxime in acid medium gives the bisulfite compound of 1,2-naphthofuroxan. In soda solution this substance is transformed into 2-nitro-1-naphthylamine-4-sulfonic acid and 2-nitro-1-naphthol-4-sulfonic acid, and in the presence of sodium hydroxide it is transformed into 1,2-naphthoquinone-4-sulfonic acid dioxime [2]. It could be assumed that the corresponding derivatives of 1,2-naphthoquinone-6-sulfonic acid dioxime will also have similar properties. Actually, the bisulfite compound of 1,2-naphthoquinone-6-sulfonic acid dioxime, obtained by the treatment of the bisulfite compound of 1-nitroso-2-naphthol-6-sulfonic acid with hydroxylamine [3], when oxidized with either nitric or nitrous acid is transformed into the bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid (I). When heated for a short time with a 1% soda solution this bisulfite compound is transformed into 2-nitro-1-naphthylamine-4,6-disulfonic acid (II), and when boiled with strong soda solution it is transformed into 2-nitro-1-naphthol-4,6-disulfonic acid (III).



(I)



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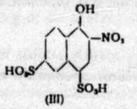
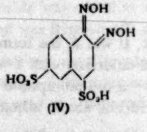
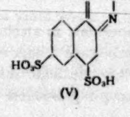


(III)

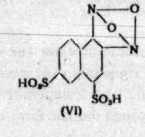
When treated with sodium hydroxide at room temperature the bisulfite compound is transformed into 1,2-naphthoquinone-4,6-disulfonic acid dioxime (IV). When reacted with weak hydrochloric acid the naphthoquinonedisulfonic acid dioxime is transformed into 2-nitroso-1-naphthol-4,6-disulfonic acid, when heated with sodium hydroxide it is transformed into 1,2-naphthofurazan-4,6-disulfonic acid (V), and when oxidized with nitric acid it is converted into 1,2-naphthofuroxan-4,6-disulfonic acid (VI):



(IV)



(V)



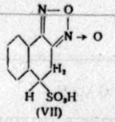
(VI)

The structure of (II) and (III) was established by the properties of their reduction products, and the structure of (IV) was established by its conversion into 2-nitroso-1-naphthol-4,6-disulfonic acid.

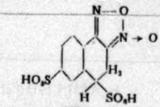
The analogous behavior of the bisulfite compounds of 1,2-naphthofuroxan and 1,2-naphthofuroxan-6-sulfonic acid shows that they are identical in structure.

If a quinoid formula with an unsymmetrical structure for the furoxan cycle is assumed for 1,2-naphthofuroxan, then the formation of 2-nitro-1-naphthylamine-4-sulfonic acid and 2-nitro-1-naphthylamine-4,6-disulfonic acid from the corresponding bisulfite compounds of 1,2-naphthofuroxan and 1,2-naphthofuroxan-6-

sulfonic acid permits assuming that the oxygen atom, not common to both of the nitrogen atoms, is found in these compounds at the nitrogen that is attached to the second carbon atom of the naphthalene nucleus (VII, VIII):



(VII)



(VIII)

EXPERIMENTAL

Bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid (I). 1) 120 ml of a solution of the bisulfite compound of 1,2-naphthoquinone-6-sulfonic acid dioxime, prepared from 0.07 mole of 1-nitroso-2-naphthol-6-sulfonic acid, was run in the course of 2 hours at 65-70° into 181 g (0.7 mole) 24.5% nitric acid and the mixture was held at 95° for 1 hour. After neutralization of the initial quantity of acid with soda, the solution was evaporated down to low bulk. The sodium nitrate which came down was filtered off and washed with methyl alcohol. The bisulfite compound of naphthofuroxansulfonic acid came down from the filtrate. The precipitate was filtered off and washed with alcohol; the yield was 12.0 g.

Under the conditions described below, we isolated 7.2 g of the sodium salt of 1,2-naphthoquinone-4,6-disulfonic acid [illegible] dioxime from the filtrate.

2) A solution of 11.57 g of the bisulfite compound of naphthoquinonesulfonic acid dioxime and 5.37 g of sodium nitrite in 30 ml of waterwas poured in the course of 1/2 hour into 78 ml of 5.6% hydrochloric acid (heated to 40°) and the mixture was held at 95° for 15 minutes. The solution was evaporated almost to dryness, the sodium chloride which came down was filtered off and washed with methyl alcohol. The residue was boiled with 100 ml of methyl alcohol, the solution was filtered and the methyl alcohol was driven off; the yield was 9.2 g. Extraction of the sodium chloride precipitates with hot methyl alcohol yielded 1 g more of product.

The sodium salt was very readily soluble in water, with more difficulty — in methyl alcohol and insoluble in ethyl alcohol; it was in the form of colorless needles (from methyl alcohol) or hexahedral prisms (from aqueous ethyl alcohol).

Found %: H_2O 12.00; C 29.95; H 1.87; Na 11.68. $C_{10}H_6O_8N_2S_2Na_2 \cdot 3H_2O$.
Calculated %: H_2O 12.12. $C_{10}H_6O_8N_2S_2Na_2$. Calculated %: C 30.61; H 1.54;
Na 11.73.

2-Nitro-1-naphthylamine-4,6-disulfonic acid (II). A solution of 22.3 g of the sodium salt of the bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid in 125 ml 1% soda solution was heated to the boil and immediately cooled to 20°. 27 g of sodium chloride was added to the solution and then 40 ml of ethyl alcohol, and the mixture was left standing for 18 hours at 18-20°. The precipitate was filtered and washed with water and alcohol; the yield was 17.3 g (74%).

The sodium salt was readily soluble in water and insoluble in alcohol, it was in the form of yellow needles (from aqueous alcohol). The diazo compound with resorcin gave a dark red color and with 1-amino-8-naphthol-3,6-disulfonic acid — a lilac color and with 2-naphthol-3,6-disulfonic acid — a red precipitate (needles). After treatment with soda, the diazo compound did not form coupling products with the above sulfonic acids but gave an intense lilac color with resorcin.

Found %: H_2O 16.31; Na 11.63. M 392.6. $C_{10}H_6O_8N_2S_2Na_2 \cdot$ 41/4 H_2O. Calculated %:
H_2O 16.33. $C_{10}H_6O_8N_2S_2Na_2$. Calculated %: Na 11.73. M 392.3.

To determine M a weighed portion of the compound was boiled with a 4.5% caustic soda solution and the ammonia was driven off into a 0.1 N hydrochloric acid solution; the excess acid was titrated with caustic soda. (Application of this method for the sodium salt of 2-nitro-1-naphthylamine-4-sulfonic acid showed that the salt contained one molecule of water).

2-Nitro-1-naphthol-4,6-disulfonic acid (III). A solution of 10.0 g of the sodium salt of the bisulfite compound of naphthofuroxansulfonic acid in 100 ml of 12.5% soda solution was boiled for 2 hours, cooled to 20° and acidified with hydrochloric acid. The sodium salt of nitronaphtholdisulfonic acid that came down was filtered off and washed with water and alcohol; the yield was 3.8 g.

The sodium salt was readily soluble in water and difficulty – in alcohol; it was in the form of yellow pyramids and bipyramids (from aqueous alcohol). Upon reduction with stannous chloride, it was converted to 2-amino-1-naphthol-4,6-disulfonic acid (long colorless needles). The action of nitric acid on the reduction product gave an orange solution which after neutralization with sodium acetate, gave a red coloration with aniline solution. Alkaline solutions gave a green coloration which turned red upon acidification. The diazo compound gave an intense fuchsine-red color with resorcin.

Found %: H_2O 16.08; Na 11.65. $C_{10}H_5O_9NS_2Na_2 \cdot 4\,1/4\,H_2O$. Calculated %: H_2O 16.29. $C_{10}H_5O_9NS_2Na_2$. Calculated %: Na 11.69.

1,2-Naphthoquinone-4,6-disulfonic acid dioxime (IV). 6.9 ml of 40.5% caustic soda solution was added to the cooled solution of 8.92 g of the sodium salt of the bisulfite compound of naphthofuroxansulfonic acid in 23 ml of water and the mixture was held at 5° for 2 hours and at 18-20° for 18 hours. The dark-red solution was acidified with hydrochloric acid and the sodium salt of naphthoquinonedisulfonic acid dioxime which came down was filtered off and washed with water and alcohol; the yield was 8.6 g (94.5%).

The sodium salt was readily soluble in water and more difficultly – in alcohol; it was in the form of light yellow trihedral prisms (from aqueous alcohol); copperas colored an aqueous solution deep dirty violet. Upon reduction with stannous chloride, it gave a compound with the properties of the sulfonic acid of 1,2-naphthylenediamine. It contained water of crystallization which did not go off at 110°; at 120-130° it was decomposed.

Found %: C 26.36; H 2.69; N 6.30; Na 10.07. $C_{10}H_6O_8N_2S_2Na_2 \cdot 3\,1/2\,H_2O$.
Calculated %: C 26.37; H 2.88; N 6.15; Na 10.10.

2-Nitro-1-naphthol-4,6-disulfonic acid. A solution of 10.5 g of the sodium salt of naphthoquinonedisulfonic acid dioxime in 65 ml of water was acidifed with 2.1 ml of 34.4% hydrochloric acid and was boiled for 2 hours. Upon addition of sodium chloride to the solution, 3.8 g of the sodium salt of the nitroso compound came down.

The sodium salt was readily soluble in water and insoluble in alcohol; it was in the form of long yellow needles (from aqueous alcohol). It gave an intense green coloration with copperas. Upon being heated with zinc in the presence of traces of acetic acid, it formed a colorless solution which rapidly turned blue, which upon acidification, turned red and upon alkalization, turned green. Reduction with stannous chloride yielded 2-amino-1-naphthol-4,6-disulfonic acid.

Found %: H_2O 8.59; Na 12.01. $C_{10}H_5O_8NS_2Na_2 \cdot 2H_2O$. Calculated %: H_2O 8.72. $C_{10}H_5O_8NS_2Na_2$. Calculated %: Na 12.20.

1,2-Naphthofurazan-4,6-disulfonic acid (V). A solution of 4.0 g of the sodium salt of naphthoquinonedisulfonic acid dioxime in 35 ml of water was alkalized with 3.5 ml of 40.5% caustic soda and boiled for 8 hours. Sodium chloride was added to the acidified solution and the sodium salt of naphthofurazandisulfonic acid came down and was filtered off; the yield was 2 g (52%).

The sodium salt was readily soluble in water and difficulty – in alcohol; it was in the form of thin curved colorless needles (from aqueous alcohol). Reduction with zinc yielded a compound with the properties of a sulfonic acid of 1,2-naphthylenediamine.

Found %: H_2O 14.55; N 6.40; Na 12.08. $C_{10}H_4O_7N_2S_2Na_2 \cdot 3\,1/2\,H_2O$. Calculated %: H_2O 14.42; N 6.41. $C_{10}H_4O_7N_2S_2Na_2$. Calculated %: Na 12.29.

1,2-Naphthofuroxan-4,6-disulfonic acid (VI). 25 ml of 56.7% nitric acid was added to a solution of 10.0 g of the sodium salt of naphthoquinonedisulfonic acid dioxime in 50 ml of water and the mixture was boiled for 10 minutes. Upon cooling the solution, the sodium salt of naphthofuroxandisulfonic acid came down; the yield was 8.1 g (79.5%).

The sodium salt was readily soluble in water and insoluble in alcohol; it was in the form of thin colorless needles (from aqueous alcohol). Reduction with zinc in the presence of hydrochloric acid and stannous chloride yielded a compound with the properties of a sulfonic acid of 1,2-naphthylenediamine.

Found %: H_2O 15.51; N 6.18; Na 9.79. $C_{10}H_4O_8N_2S_2Na_2 \cdot 4\ H_2O$. Calculated %: H_2O 15.59; N 6.06; Na 9.95.

SUMMARY

1. The oxidation of the bisulfite compound of 1,2-naphthoquinone-6-sulfonic acid dioxime with either nitric or nitrous acid leads to the bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid.

2. When treated with soda the bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid is transformed into either 2-nitro-1-naphthylamine-4,6-disulfonic acid or into 2-nitro-1-naphthol-4,6-disulfonic acid, and when treated with sodium hydroxide at room temperature it is converted into 1,2-naphthoquinone-4,6-disulfonic acid dioxime.

3. In acid medium 1,2-naphthoquinone-4,6-disulfonic acid dioxime is transformed into 2-nitroso-1-naphthol-4,6-disulfonic acid, into 1,2-naphthofurazan-4,6-disulfonic acid when heated with sodium hydroxide, and into 1,2-naphthofuroxan-4,6-disulfonic acid when oxidized with nitric acid.

4. The transformations of the bisulfite compound of 1,2-naphthofuroxan-6-sulfonic acid in alkaline medium are analogous to the transformation of the bisulfite compound of 1,2-naphthofuroxan.

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Dyes

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* T. p. = C. B. Translation pagination.

CATALYTIC CONDENSATION OF ACETYLENE WITH AROMATIC AMINES

XXV. SYNTHESIS OF 2-(HYDROXYPHENYL)QUINOLINE DERIVATIVES

N. S. Kozlov and L. Yu. Pinegina

A new method for the synthesis of 2-phenylquinoline derivatives, proceeding from acetylene, aromatic amines and aromatic aldehydes, was described in some earlier studies made by one of us [1-3]. This communication is a further development of the indicated investigations. Here we studied the catalytic condensation of acetylene and primary aromatic amines with salicylaldehyde. The aromatic amines taken for reaction were aniline, o-, m- and p-toluidines, m-xylidine, o- and p-anisidines, and, finally, p-phenetidine.

Based on our studied reaction we synthesized 2-(2'hydroxyphenyl)quinoline and its derivatives, and specifically: 2-(2'-hydroxyphenyl)-6-methylquinoline, 2-(2'-hydroxyphenyl)-7-methylquinoline, 2-(2'-hydroxyphenyl)-8-methylquinoline, 2-(2'-hydroxyphenyl)-6,8-dimethylquinoline, 2-(2'-hydroxyphenyl)-6-methoxyquinoline, 2-(2'-hydroxyphenyl)-8-methoxyquinoline, and, finally, 2-(2'-hydroxyphenyl)-6-ethoxyquinoline. With the exception of the first compound, all of the others have not been described in the literature up to now. The present study extended the sphere of using the condensation reaction of acetylene and primary aromatic amines with aromatic aldehydes, and it was shown that the hydroxy derivatives of aromatic aldehydes can also be introduced into this reaction.

At the same time we developed a new method for the direct synthesis of hydroxy derivatives of 2-phenylquinoline with the hydroxyl group being on the phenyl radical. As is known, up to now these compounds have been obtained by a more complicated method consisting of several stages – most frequently by the diazotization of the corresponding amino derivatives, or by the alkaline fusion of the corresponding phenylquinolinesulfonic acids [5], or, finally, by the decarboxylation of the corresponding hydroxyphenylquinolinecarboxylic acids [6].

EXPERIMENTAL

All experiments of the co-condensation of aromatic amines with aromatic aldehydes and acetylene were performed by the following scheme. The aromatic amine and the aromatic aldehyde were taken in the molar ratio of 1.5 : 1, mercuric chloride served as the catalyst and the solvent was ethyl alcohol. The reaction mass was saturated with acetylene in the cold, or, if the intermediate reaction product (Schiff base) was difficulty soluble in cold alcohol, with heating to 70-80°. After the reaction mass was completely saturated with acetylene, a 10% soda solution was added to the reaction product (until it gave an alkaline reaction) in order to destroy the remains of the catalyst. The reaction mass was then treated with steam and the solvent (alcohol) was driven off with a small quantity of the unreacted aromatic amine.

The reaction product in all cases was a resinous mass, most often, brown in color. This resin was vacuum-distilled (3-4 mm). The first fraction as a rule consisted mainly of the intermediate reaction product – the Schiff base. The second fraction which contained the quinoline base was studied in detail. The second fraction crystallized most of the time and upon recrystallization, it yielded the pure reaction product. In those cases when the second fraction did not crystallize, the quinoline base was extracted from it through a complex with ferrocyanic acid which was then decomposed by alkali. The quinoline base was extracted from the alkaline solution with ether and then crystallized from alcohol.

Synthesis of 2-(2'-hydroxyphenyl)-quinoline. We took 30 g salicylaldehyde, 37.5 g aniline, 100 ml ethyl alcohol and 4 g mercuric chloride. The mixture was saturated with acetylene in the course of 24 hours. We obtained 48 g of resin. 12 g was distilled in vacuum (3 mm): the 1st fraction boiled at 100-150°, 3.3 g; the 2nd fraction boiled at 150-170°, 6.0 g; the residue was 2.5 g. From the 2nd fraction we obtained yellow crystals, m.p. 115°, which corresponded to the literature data for 2-(2'-hydroxyphenyl)-quinoline [7]. The picrate melted at 184-185°. The yield of 2-(2'-hydroxyphenyl)-quinoline was 4.75 g (35.0%).

Found %: C 81.54, 81.46; H 4.96, 4.89; N 6.43. $C_{15}H_{11}ON$. Calculated %: C 81.44; H 4.98; N 6.34.

Analysis of the platinate: Found %: Pt 22.60. $C_{30}H_{24}O_2N_2Cl_6Pt$. Calculated %: Pt 22.97.

Synthesis of 2-(2'-hydroxyphenyl)-6-methylquinoline. We took 30 g salicylaldehyde, 42.9 g p-toluidine, 100 ml of ethyl alcohol and 7 g mercuric chloride. The mixture was saturated with acetylene in the course of 25 hours. We obtained 52.2 g resin of which 15 g was vacuum-distilled (3 mm): the 1st fraction boiled at 110-200°, 3.3 g; the 2nd fraction at 200-235°, 5.9 g; the residue was 5.6 g; the losses – 0.2 g. From the 2nd fraction we isolated 5.1 g reaction product (34.2%). It was in the form of yellow crystals, m.p. 144-145°. The prepared picrate melted at 216-217° (decomp.) and we also prepared the platinate.

Found %: C 81.87, 81.59; H 5.73, 5.88; N 5.97, 6.16. $C_{16}H_{31}ON$. Calculated %: C 81.70; H 5.53; N 5.96.

Analysis of the platinate: Found %: Pt 22.12, 22.27. $C_{32}H_{28}O_2N_2Cl_6Pt$. Calculated %: Pt 22.24.

Synthesis of 2-(2'-hydroxyphenyl)-7-methylquinoline. We took 10.8 g salicylaldehyde, 15.5 g m-toluidine, 40 ml ethyl alcohol and 3 g mercuric chloride. The mixture was saturated with acetylene in the course of 20 hours. We obtained 29.3 g resin of which 10 g was vacuum-distilled (1 mm): the 1st fraction boiled at 105-160°, 3 g; the 2nd at 160-190°, 3.4 g; the residue was 3.5 g; the losses – 0.1 g. From the 2nd fraction we isolated 3 g (38.6%) of reaction product. It was in the form of yellow acicular crystals, m.p. 126-127°. The picrate melted at 196-196° (decomp.).

Found %: C 81.96; 81.64; H 5.69, 5.69. $C_{16}H_{13}ON$. Calculated %: C 81.70; H 5.53; N 5.96.

Analysis of the platinate: Found %: Pt 22.17. $C_{32}H_{28}O_2N_2Cl_6Pt$. Calculated %: Pt 22.24.

Synthesis of 2-(2'-hydroxyphenyl)-8-methylquinoline. We took 30 g of salicylaldehyde, 42.9 g o-toluidine, 100 ml ethyl alcohol and 7 g mercuric chloride. The reaction mixture was saturated with acetylene in the course of 23 hours. We obtained 61.6 g resin of which 15 g was vacuum-distilled (3 mm): the 1st fraction boiled at 100-160°, 3.8 g; the 2nd fraction at 160-200°, 6.2 g; the residue was 4.8 g; the losses – 0.2 g. From the 2nd fraction we isolated 4 g (28.5%) of reaction product. It was in the form of yellow needles, m.p. 101-102°. The picrate melted at 194-195°.

Found %: C 81.74, 81.83; H 5.80, 5.64; N 5.86, 6.14. $C_{16}H_{13}ON$. Calculated %: C 81.70; H 5.53; N 5.96.

Analysis of the platinate. Found %: Pt 22.51, 22.44. $C_{32}H_{28}O_2N_2Cl_6Pt$. Calculated %: Pt 22.24.

Synthesis of 2-(2'-hydroxyphenyl)-6-methoxyquinoline. We took 30 g salicylaldehyde, 65.9 g p-anisidine, 200 ml ethyl alcohol, 7 g mercuric chloride. The reaction mixture was saturated with acetylene in the course of 25 hours. We obtained 68.6 g resin of which 11 g was vacuum-distilled (3 mm): the 1st fraction boiled at 90-200°, 1.8 g; the 2nd fraction at 200-240°, 6.4 g; the residue was 2.6 g; the losses – 0.2 g. From the 2nd fraction we isolated 5.9 g (51.6%) of reaction product. It was in the form of yellow crystals, m.p. 159°. The picrate melted at 188-189°.

Found %: C 76.63, 76.36; H 5.34, 5.48; N 5.56, 5.74. $C_{16}H_{13}O_2N$. Calculated %: C 76.49; H 5.37; N 5.57.

Analysis of the platinate: Found %: Pt 21.09, 21.44. $C_{32}H_{28}O_4N_3Cl_6Pt$. Calculated %: Pt 21.45.

Synthesis of 2-(2'-hydroxyphenyl)-8-methoxyquinoline. We took 9 g salicylaldehyde, 20 g o-anisidine, 60 ml ethyl alcohol and 5 g mercuric chloride. The mixture was saturated with acetylene for

18 hours. We obtained 20.7 g of resin of which 20 g was vacuum-distilled (3 mm): the 1st fraction boiled at 120-215°, 6.2 g; the second fraction at 215-260°, 6.2 g; the residue was 7.2 g; the losses − 0.3 g. From the 2nd fraction we isolated 3.6 g (20.1%) of reaction product. It was in the form of yellow crystals, m.p. 154-155°. The prepared picrate melted at 221° (decomp.).

Found %: N 5.42, 5.35. $C_{16}H_{13}O_2N$. Calculated %: N 5.58.

Analysis of the platinate. Found %: Pt 21.47. $C_{32}H_{28}O_4N_2Cl_6Pt$. Calculated %: Pt 21.45.

Synthesis of 2-(2'-hydroxyphenyl)-6-ethoxyquinoline. We took 24.5 g salicylaldehyde, 41.3 g of p-phenetidine, 100 ml of ethyl alcohol and 5 g of mercuric chloride. The reaction mixture was saturated with acetylene in the course of 22 hours. We obtained 59.5 g of resin of which 16.8 g was vacuum-distilled (1-2 mm); the 1st fraction boiled at 100-210°, 2 g; the second at 210-230°, 6.7 g; the residue was 8.0 g; the losses − 0.1 g. From the 2nd fraction we isolated 5.7 g (34.2%) of reaction products. It was in the form of yellow crystals, m.p. 153°. The picrate decomposed without melting at 200°.

Found %: C 76.79, 76.94; H 5.54, 5.43; N 5.63, 5.60. $C_{17}H_{15}O_2N$.
Calculated %: C 76.98; H 5.66; N 5.28.

Analysis of the platinate. Found %: Pt 20.95, 20.77. $C_{34}H_{32}O_4N_2Cl_6Pt$. Calculated % Pt 20.81.

Synthesis of 2-(2'-hydroxyphenyl)-6,8-dimethylquinoline. We took 10 g salicyladehyde, 15 g m-toluidine, 60 ml ethyl alcohol and 7 g mercuric chloride. The reaction mixture was saturated with acetylene in the course of 15 hours. We obtained 24.2 g resin of which 13.3 g was vacuum-distilled (3 mm): the 1st fraction boiled at 90-185°, 4.6 g; the 2nd fraction at 185-220°, 4.6 g; the residue was 3.8 g. 3.9 g (37.5%) of reaction product was obtained from the second fraction. The product was in the form of dark yellow coarse crystals, m.p. 124-125°. The picrate melted at 204-205° (decomp.).

Found %: C 82.33, 82.19; H 6.08, 6.11; N 5.75, 5.47. $C_{17}H_{15}ON$. Calculated %: C 81.93; H 6.02; N 5.62.

Analysis of the platinate. Found %: Pt 21.68, 21.47. $C_{34}H_{32}O_2N_2Cl_6Pt$. Calculated %: Pt 21.55.

SUMMARY

1. The catalytic condensation of salicylaldehyde and a number of aromatic amines with acetylene was studied.

2. A new method was developed for the direct synthesis of hydroxy derivatives of 2-phenylquinoline in which the hydroxyl group is on the phenyl radical. Seven new compounds were synthesized in this series.

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THE ACID CHLORIDES OF PARTIAL AROMATIC ESTERS OF ARYLSULFONIMIDOPHOSPHORIC ACIDS

A. V. Kirsanov and V. I. Shevchenko

The acid chlorides of the partial esters of arylsulfonimidophosphoric acids of the type $ArSO_2N{=}PCl_2(OR)$ (I) and $ArSO_2N{=}PCl(OR)_2$ (II) are of interest, since they can be used as intermediates, in particular, for the preparation of mixed esters of arylsulfonimidophosphoric acids [1].

We were unable to obtain the (I) and (II) types of compounds by reacting trichlorophosphazosulfonaryls with phenols. By reacting the sodium salt of N-chlorobenzenesulfonamide with phenylphosphite dichloride (cf. [1, 2]) we were able to obtain the phenylsulfonimidophosphoric acid phenyl ester dichloride (III) in accord with the scheme:

$$C_6H_5SO_2NNaCl + PCl_2(OC_6H_5) \longrightarrow C_6H_5SO_2N{=}PCl_2(OC_6H_5) + NaCl.$$

When (III) is treated with 2 moles of sodium phenolate it gives the triphenyl ester of phenylsulfonimidophosphoric acid in good yield, which proves its structure.

The methyl- and ethylphosphite dichlorides also react readily with the sodium salt of N-chlorobenzenesulfonamide, but here compounds of type (I) and (II) fail to be formed (cf. EXPERIMENTAL).

Considerably better results were obtained when we reacted the sodium salt of N-chlorobenzenesulfonamide with the monochlorides of the aromatic esters of phosphorous acid. Thus, for example, the reaction of the sodium salt of N-chlorobenzenesulfonamide with diphenylphosphite chloride gives in good yield the crystalline phenylsulfonimidophosphoric acid diphenyl ester chloride:

$$C_6H_5SO_2NNaCl + PCl(OC_6H_5)_2 \longrightarrow C_6H_5SO_2N{=}PCl(OC_6H_5)_2 + NaCl.$$

With sodium phenolate the phenyl sulfonimidophosphoric acid diphenyl ester chloride gives the triphenyl ester. The chloride is easily hydrolyzed by dilute sodium hydroxide solutions. Acidification of the alkaline hydrolyzate results in the precipitation of the partial diphenyl ester of phenylsulfonamidophosphoric acid, identical with the diphenyl ester obtained from either the dichloride of the acid and sodium phenolate or by the saponification of the triphenyl ester [3].

The acid chlorides of the o-, m- and p-cresylphenylphosphites also react readily with the sodium salt of N-chlorobenzenesulfonamide to give liquid acid chlorides of the cresylphenyl esters of phenylsulfonimidophosphoric acid. Their structure is shown by the fact that they give the corresponding partial cresylphenyl esters of phenylsulfonamidophosphoric acid in crystalline form and in good yields (65-86%).

The hydrolysis of the monochlorides proceeds in accord with the scheme:

$$C_6H_5SO_2N{=}PCl(OAr)_2 + H_2O \longrightarrow C_6H_5SO_2NHPO(OAr)_2 + HCl.$$

Titration of the hydrolysis products is a rapid and convenient analysis method. The acid chlorides of the diaryl esters of phenylsulfonimidophosphoric acid titrate as two equivalents of acid (to phenolphthalein). The acid chlorides are hydrolyzed very slowly by cold water.

To obtain the phenylcresyl esters the acid chlorides were hydrolyzed in alkaline medium. Acidification of the alkaline hydrolyzate gave the partial phenylcresyl esters as an oily layer that soon crystallized.

The mixed partial esters are colorless crystalline substances with a very bitter taste. Chemically they are monobasic acids, with dilute sodium hydroxide solution titrating as one equivalent (to phenolphthalein). Like the other partial esters described earlier [3, 4], they are stable to both dilute alkali and mineral acid solutions.

EXPERIMENTAL

Reaction of the sodium salt of N-chlorobenzenesulfonamide with phenylphosphite dichloride. To carry out the reaction it is necessary to add chloroamide to the phosphorus-containing compound and not the reverse. Moreover, it is necessary to avoid an excess of chloramide since it readily reacts with the reaction product. If an excess of chloramide is used, the yield of triphenyl ester formed by the reaction of the reaction product with sodium phenolate is reduced.

Portions of 0.03 mole of the sodium salt of the N-chlorobenzenesulfonamide, ground to a fine powder, were added to a solution of 0.03 mole of the phosphoric acid phenyl ester dichloride in 50 ml of carbon tetrachloride. The temperature of the reaction mixture was held in the range of 30-40°. The reaction went rapidly and readily. The sodium chloride was separated off and washed with a small quantity of carbon tetrachloride. The filtrate was steamed down; the solvent was driven off in vacuum on a water bath. After the solvent had been driven off, a thick oily liquid remained. The yield of phenylsulfonimidophosphoric acid monophenyl ester dichloride was 9.76 g (92.9%).

Found: equiv. of acid on hydrolysis* 3.93, 3.96. $C_{12}H_{10}O_3NSPCl_2$. Calculated: equiv. 4.00.

Reaction of phenylsulfonimidophosphoric acid phenyl ester dichloride with sodium phenolate. 0.10 mole sodium phenolate was added to a solution of 0.005 mole phenylsulfonimidophosphoric acid phenyl ester dichloride in 15 ml of benzene. The reaction was energetic and the sodium phenolate dissolved. To isolate the triphenyl ester of phenylsulfonimidophosphoric acid, the benzene was driven off from the reaction mixture under reduced pressure on a water bath. 50 ml of water was added to the residue. The oily layer which formed was treated with 0.2 N caustic soda solution, washed with water, dissolved in ether and dried with calcium chloride. After the ether was driven off, we obtained the readily crystallized triphenyl ester. The yield was 1.68 g (72.4%). After crystallization from alcohol, it melted at 85-87°. A mixture test with the triphenyl ester prepared from trichlorophosphazosulfonphenyl and sodium phenolate gave no melting point depression.

Reaction of methyl- and ethylphosphite dichlorides with the sodium salt of N-chlorobenzenesulfonamide. The methyl- and ethylphosphite dichlorides very readily react with the sodium salt of N-chlorobenzenesulfonamide to form a colorless, non-crystallizable and non-distilling (without decomposition) liquid with the odor of the initial acid chloride. This liquid, upon reaction with the corresponding sodium alcoholates, does not yield readily isolated and identifiable trialkyl esters of arylsulfonimidophosphoric acids [4] and, therefore contains no acid chlorides of type (I). In all probability, the initially formed acid chlorides of type (I) immediately react with the sodium salts of chloramide, to form more complex product and a portion of the initial acid chloride remains unchanged. This hypothesis is supported by the fact that the monophenyl ester of phenylsulfonimidophosphoric acid dichloride also readily reacts with chloramide (see above).

Preparation of phenylsulfonimidophosphoric acid diphenyl ester chloride. 0.03 mole of the phosphorus acid diphenyl ester chloride was dissolved in 50 ml of carbon tetrachloride. The solution was heated to 30-40° and 0.03 mole of the anhydrous sodium salt of the N-chlorobenzenesulfonamide, ground to a fine powder, was added in portions to the above solution. The reaction went very readily and all of the chloramide reacted. The reactants may be mixed in the reverse order: a solution of 0.03 mole of diphenylphosphite chloride in 30 ml of carbon tetrachloride was added with stirring, through a dropping funnel to a mixture of 0.03 mole of chloramide and 20 ml of carbon tetrachloride; the addition was at such a rate so that the temperature of the reaction mixture stayed in the range of 30-40°. The sodium chloride was separated off , the filtrate was evaporated down, and the solvent was driven off in vacuum over a boiling water bath. As the residue we obtained a crystalline mass or a viscous liquid which, upon cooling with ice water, solidified. The yield of crude product was 11.0 g (90.1%). For purification, the acid chloride was crystallized from carbon tetrachloride; it was in the form of fine colorless prisms that melted at 66-69°. The acid chloride was readily soluble in alcohol, acetone, benzene; in water it was insoluble and slowly hydrolyzed.

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* Here and below – phenolphthalein.

Found: equiv. acid upon hydrolysis: 2.00, 2.03. $C_{18}H_{15}O_4NSPCl$. Calculated: equiv. 2.00.

Reaction of phenylsulfonimidophosphoric acid diphenyl ester chloride with sodium phenolate. 0.005 mole of sodium phenolate was added to a solution of 0.005 mole diphenyl ester of phenylsulfonimidophosphoric acid chloride in 10 ml of carbon tetrachloride, which was previously heated to 50°. The sodium phenolate readily reacted with the acid chloride. To isolate the triphenyl ester, the reaction mixture was evaporated down, and the solvent was driven off in vacuum on a water bath. 30 ml of water was added to the residue. Upon rubbing with a small glass rod, an oil formed which was easily crystallized. The crystalline precipitate was separated off, washed with water and dried. The yield was 2.16 g (93.1%). After crystallization from alcohol, it melted at 85-86°. A mixture test with the triphenyl ester of phenylsulfonimidophosphoric acid, prepared from trichlorophosphazosulfonphenyl and sodium phenolate, gave no melting point depression.

Hydrolysis of phenylsulfonimidophosphoric acid diphenyl ester chloride. 10 ml of 1 N caustic soda solution was added to 0.01 mole diphenyl ester of phenylsulfonimidophosphoric acid chloride and the mixture was heated until the acid chloride completely dissolved. The solution was filtered and acidified with 2 N hydrochloric acid solution until an acid reaction was obtained with congo. The acid diphenyl ester of phenylsulfonamidophosphoric acid which came down was separated, washed, and crystallized from alcohol, m.p. 144-145°. A mixture test with the diphenyl ester of phenylsulfonamidophosphoric acid prepared by hydrolysis of the triphenyl ester or from the acid dichloride and sodium phenolate [3] gave no melting point depression.

Preparation of phenylsulfonimidophosphoric acid cresylphenyl ester chlorides. 0.01 mole of powdered sodium salt of the benzenesulfonic acid chloride was added to a solution of 0.01 mole cresylphenyl ester of phosphoric acid chloride in 5 ml of carbon tetrachloride. The reaction went very readily and the chloramide rapidly disappeared. 20 ml of carbon tetrachloride was added to the reaction mixture and it was left standing for several hours to coagulate the sodium chloride. After separation of the sodium chloride, the filtrate was steamed down and the solvent was driven off under reduced pressure over a water bath. The cresylphenyl ester of phenylsulfonimidophosphoric acid chloride was obtained from the residue in the form of a viscous, noncrystallizable oily liquid.

All the prepared acid cresylphenyl ester chlorides were colorless liquids, miscible in benzene, alcohol, ether and acetone. In water they were insoluble and slowly hydrolyzed. In order to identify the acid chlorides, they were converted to readily crystallized acid cresyl esters.

The yield of o-cresylphenyl ester of phenylsulfonimidophosphoric acid chloride was 3.97 g (94.3%).

Found: equiv. of acid during hydrolysis 1.99, 1.98. $C_{19}H_{17}O_4NSPCl$. Calculated: equiv. 2.00.

The m-cresylphenyl ester of phenylsulfonimidophosphoric acid chloride was obtained in a yield of 4.06 g (96.5%).

Found: equiv. of acid on hydrolysis 2.01, 1.99. $C_{19}H_{17}O_4NSPCl$. Calculated: equiv. 2.00.

The yield of p-cresylphenyl ester of phenylsulfonimidophosphoric acid chloride was 3.88 g (92.0%).

Found: equiv. of acid during hydrolysis 1.91. $C_{19}H_{17}O_4NSPCl$. Calculated: equiv. 2.00.

Preparation of the acid cresylphenyl esters of phenylsulfonamidophosphoric acid. 20 ml of 1 N caustic soda solution was added to 0.01 mole of acid cresylphenyl ester chloride and the mixture was heated until the acid chloride dissolved. The solution was filtered and acidified with hydrochloric acid until there was an acid reaction with congo. The acid cresylphenyl esters of phenylsulfonamidophosphoric acid came down in the form of a viscous oily layer which gradually crystallized. The precipitate was separated and well washed with water and dried. For purification, the product was crystallized from dilute alcohol (65%) or carbon tetrachloride.

The yield of the o-cresylphenyl ester of phenylsulfonamidophosphoric acid was 3.47 g (86.1%). It readily dissolved in acetone, benzene and difficultly – in hot water. It was crystallized from alcohol in the form of transparent fine prisms, m.p. 112-114°.

Found %: N 3.48. Equiv. 0.981, 0.993. $C_{19}H_{18}O_5NSP$. Calculated %: N 3.47. Acid equiv. 1.00.

The m-cresylphenyl ester of phenylsulfonamidophosphoric acid was obtained in a yield of 3.28 g (81.3%). It was very readily soluble in acetone, chloroform, alcohol, benzene, hot carbon tetrachloride and difficultly soluble in hot water and in cold carbon tetrachloride. From dilute alcohol it came down in the form of fine platelets, m.p. 117-120°.

Found: equiv. 0.979, 0.990. $C_{19}H_{18}O_5NSP$. Calculated: equiv. 1.00.

The yield of the p-cresylphenyl ester of phenylsulfonamidophosphoric acid was 2.61 g (64.5%). The ester was readily soluble in acetone, alcohol, benzene, hot carbon tetrachloride and in petroleum ether. From alcohol it came down in the form of platelets (often in the form of regular hexahedrons), m.p. 128-129°.

Found: equiv. 0.913, 1.02. $C_{19}H_{18}O_5NSP$. Calculated: equiv. 1.00.

SUMMARY

1. The acid chlorides of some partial aromatic esters of arylsulfonimidophosphoric acids were prepared.
2. Some mixed partial aromatic diesters of arylsulfonamidophosphoric acids were prepared.

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* T. p. = C. B. Translation pagination.

THE GENERAL DEFINITION OF CHEMICAL SCIENCE

(A DISCUSSION)

Yu. A. Zhdanov

Is it necessary to be concerned with the most precise definition of scientific concepts? An affirmative reply to this question is not always given. There are some scientific workers who do not consider it too essential. It is impossible to agree with such a viewpoint. A vagueness in defining scientific ideas can lead to superfluous debates on terminology, to the lack of indispensable clarity in scientific thinking, and breeds confusion during discussion. Also, it is impossible to permit specialists in chemistry to employ vague and subjective descriptions of chemistry, organic chemistry, valency, protein, etc.

To be sure, the problem is complicated by a number of important considerations. Firstly, in connection with the general development of science, applicability and scope of the various ideas change. Secondly, nature fails to recognize any sharp metaphysical boundaries between phenomena, which leads to the difficulty of sharply defining certain ideas. Thirdly, at times the human mind does not keep step with the actual level of science and lacks concepts that correlate the new data of research and practice. But all of these difficulties do not eliminate the need for achieving clarity in defining scientific concepts and terminology.

In this connection it is expedient to consider a certain lack of clarity that exists in the general definition of chemistry as a science. Chemistry is usually defined as a science of substances and their transformations. Expressed in such simple terms, this formulation is essentially very inexact. As a matter of fact the changes in the state of aggregation of bodies, many polymorphous transfomations, radioactive decomposition, etc., are directly associated with the transformations of substances; however, they are not within the exclusive jurisdiction of chemistry. The inexactness of the presented definition is due to the fact that it describes, only in general terms, phenomena that are characteristic of chemical activity, without discussing their nature. Marx [1] wrote – "If the phenomena of chemistry and their causes were the same, then all science would be superfluous". Since the phenomena of chemical activity and their causes are separate, the presented definition of chemistry, by ignoring this circumstance, must be called pragmatic rather than scientific.

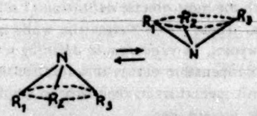
In defining chemistry as a science, we proceed from the known definition given by F. Engels in "Dialectics of Nature": "Chemistry can be called the science of qualitative changes in bodies, which take place in conformity with changes in their quantitative composition" [2]. The thought expressed here by Engels is confirmed by the hundreds of thousands of examples from the domain of inorganic and organic chemistry, where the cited dialectical law manifests itself with astounding vigor.

Together with this, the chemist cannot disregard the fact that the indicated definition fails to embrace the numerous cases of isomerism, shown for both organic and inorganic compounds. As a matter of fact, in isomeric transformations, the quantitative composition of substances fails to change, but still they can show decided differences among themselves in fundamental and qualitative properties.

To be sure, this does not mean that the general dialectical rule on the transition of quantitative changes into qualitative changes fails to appear in isomerization phenomena. Engels, having indicated in his work "Dialectics of Nature" the manifestation of this dialectical law in homologous series of chemical compounds, stated: "Besides the other, in these series, the Hegelian law appears before us in still another form. The lower members of the series permit only a single mutual arrangement of the atoms. But if the number of atoms combining in a molecule reaches a certain definite value for each series, then the grouping within the molecule can occur in several ways; as a result, two or several isomers can appear, that contain in their molecules the same number of C, H and O atoms, but at the same time showing qualitative differences between themselves. We are even in a position to calculate the number of like isomers possible for each member of the series. Thus, in the paraffin series there exist two isomers for C_4H_{10}, and three for C_5H_{12}: for the higher members, the number of possible isomers increases very rapidly. As a result, the number of atoms in the molecule again determines the possibility and also – to the extent that it is shown experimentally – the actual existence of similar but qualitatively different isomers" [3].

What actually determines the possibility of several isomers existing by transformation? As a matter of fact, we can depict the molecule as being an externally closed, but internally disordered, instantaneously changing conglomerate of atoms. In such case there could be no discussion as to the existence of isomers, as there fail to be, for example, an infinite number of stable revolving isomers for ethane CH_3-CH_3, although they could be depicted as being individual spatial groupings of atoms.

Where there is an insufficiently stable arrangement of the atoms, the theoretically predicted isomers also fail to appear. Thus, amines of type $N_{41}R_2R_3$ have a tetrahedral structure and by analogy with carbon compounds of type $CR_1R_2R_3R_4$ should show optical isomerism. Actually this is not the case, since the flattened tetrahedron of such amines is easily turned inside out, similar to an umbrella:



The possibility for the existence of different isomers becomes real as the result of molecules possessing a special property: a constant (stable) order of interaction for the atoms contained in them, i.e. structure.

As is known, the school of thought by A. M. Butlerov on the chemical structure of molecules was based first on the phenomenon of isomerization. "Not being known, isomers were not studied – there was no need for 'structure', but that time has long since passed . . . . "[4].

However, a structure is also possessed by molecules that do not have isomers. Structure is a fundamental property of molecules, and one of its particular manifestations is the presence of isomeric substances with the same chemical composition. Chemical structure means first a definite order of interaction for the atoms in molecules, in which connection, as was emphasized by Butlerov, the interaction is dynamic. In chemistry the specific form of material motion appears as a change in this structure during chemical reactions.

It is necessary to emphasize that chemical structure is not confined to a spatial grouping of atoms. The doctrine of chemical structure takes into consideration the whole complex problem of the character of atomic reactivity in molecules, including in this number also the mutual influence of distant atoms and radicals.

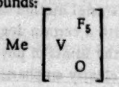
The doctrine of chemical structure was originally applied to substances having a molecular structure. Butlerov very definitely emphasized this fact: "In a word, I assert that an understanding of chemical structure is valid in all those cases where a strict understanding prevails of the nature of the chemical particles of substances. Together with the latter it stands, and together with the latter it falls. It is impossible to extend the concept of chemical structure to all substances without exception, just as it is impossible to extend to all of them the concept of chemical particles" [5].

The caution that Butlerov displayed here is fully explained by the state of science at the time. Now, in connection with the development of powerful methods of investigation, it has become possible to study the structure of bodies that are not composed of separate molecules. In this category belong many liquid and solid solutions, diverse crystalline bodies, polymers, etc.

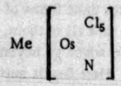
The successes achieved in the study of the structure of bodies led to the astonishing conclusion that in certain cases and within certain limits, the quantitative composition of bodies is determined by the structure. From school we are familiar with the example of the formation of iron sulfide FeS from sulfur and iron as being proof for the validity of the law of constant composition and the law of multiple proportions. However, in reality, the composition of iron sulfide is close to Fe_8S_7 or $Fe_{11}S_{12}$. The slight lack of iron is explained by the fact that some of the positions in the crystalline lattice of the sulfide prove to be unoccupied.

Numerous facts from the domain of the chemistry of silicates led Academician Fersman to the following important conclusion: "That the lattice determines the most important phenomena of chemical composition can be seen from the fact that, for example, in hornblendes there exists a certain excess of oxygen with respect to the stoichiometric formula, which is explained by the need of supplying some unsaturated bonds in the metasilicate chain when atoms of different valency are substituted; from the purely chemical viewpoint it is quite evident that to assume slightly more than 3 oxygen atoms for a compound of the type of $MgSiO_3$ is absurd and a contradiction of the fundamental laws of chemical compounds, and, in addition, the very fine analyses of recent times have shown that a very slight excess of either O or F is present in such compounds (which, because of the closeness of the ionic radii of oxygen and fluorine, is fully understandable)" [6].

In some cases it would seem that the conditions, imposed by the requirements of structure, essentially change the fundamental characteristics of atoms. In support of this thought, reference can be made, for example, to the following interesting compounds:



$\mathrm{Me}\left[\mathrm{V}\begin{array}{c}\mathrm{F_5}\\ \mathrm{O}\end{array}\right]$



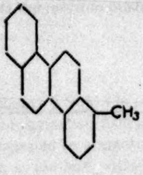
$\mathrm{Me}\left[\mathrm{Os}\begin{array}{c}\mathrm{Cl_5}\\ \mathrm{N}\end{array}\right]$

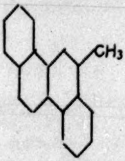
In the first case the coordination capacity of normally divalent oxygen corresponds to that of monovalent fluorine, while in the case of the pentachloroosmic acid the role of a monovalent group is played by trivalent nitrogen.

At times it would seem that substances, in order to comply with the requirements of structure, show striking change in their fundamental properties. The enormous chemical and physical differences of such compounds as H_2S, HCOOH, CH_3OH are obvious to all. However, with hydroquinone these compounds all form crystalline products that are very close in properties and have the same composition $3C_6H_4(OH)_2 \cdot M$, where M is one of the mentioned substances. The composition of these (the so-called clathrate) compounds is determined by the structure of the hydroquinone lattice, in the voids of which, the same as in a cell, the molecules of the ensnared substances are held.

A large number of compounds of variable composition (mutable, as they were called by Fersman) are known, especially among the aluminosilicates and polymers, for which the structure proves to be the most important characteristic, and an elucidation of structure, the most important problem. Here the question is complicated by the fact that in many cases the compounds are not composed of molecules, but of endless linear, planar or spatial systems, where the same structural elements fail to always show strict repetition, by which the elements could be placed in at least some sort of relationship to molecules.

In an enormous number of cases the structure, when compared with the quantitative composition, proves to be the decisive factor, determining the most important properties of substances. It is difficult to reduce to a transition of quantitative changes into qualitative differences, in the properties, for example, of the following methylchrysenes:





The first substance is a carcinogenic compound, while the second is practically harmless in this respect.

In this connection the important statement made by Engels should be borne in mind: "In physics, and even more so in chemistry, not only does constant qualitative change take place as the result of quantitative changes, i.e. transition of quantity into quality, but it also becomes necessary to examine the multitude of such qualitative changes, the causation of which by quantitative change has completely failed to be established. There can be ready agreement with the fact that the contemporary tendency in science moves in that direction, but this does not prove that it is exclusively correct and that, following this tendency, we in the end will exhaust both physics and chemistry" [7].

Various physical disciplines, other than chemistry, study the structure of matter; here the operational spheres of physics and chemistry are frequently tightly interwoven. At the junctions between these sciences there rapidly develop intermediate branches of knowledge (physical chemistry, colloid chemistry, radiation chemistry, etc.). Under the influence of various external factors it becomes possible to produce different changes in the state of bodies: to achieve luminescence or to erect a dipole, to endow molecules with a charge or to change the state of aggregation. However, if here the structure of the body fails to change, then we still find ourselves in the realm of chemistry. The transformations of atomic nuclei lie outside the bounds of chemistry, although these transformations naturally lead to a change in the chemical properties of atoms, and consequently to a change of their relationships, i.e. to chemical reactions.

Having given the fundamental characteristic of the chemical form of motion, Engels indicated the path that should be followed in searching for a more complete definition of chemistry as a science. In a letter to Marx he states that physics investigates those forms of material motion such as heat, light, electricity and magnetism, "and in conclusion finds that all of them, with a certain degree of intensity that changes for different moving bodies, produce effects, which go beyond the limits of physics, changing the internal structure of bodies, i.e. chemical effects" [8]. Here Engels quite clearly emphasizes that chemical changes are chiefly a change in the internal structure of bodies.

In accord with this statement, based on the observation of actual facts and confirmed by the whole grandiose development of knowledge on the structure of chemical compounds, it follows that the subject of chemistry should be defined as befits a science. Apparently, chemistry is the science of the qualitative changes of bodies that occur under the influence of changes in their quantitative composition and structure.

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AMINO ACID AMIDINES OF THE DIHYDROPYRAZINE SERIES

I. PREPARATION FROM THE IMINO ETHER OF (O,O-DIBENZYL-2,5-DIHYDROPYRAZINE) AMIDINES

R. G. Petrova and N. I. Gavrilov

One of the best methods for the preparation of aliphatic and aromatic linear amidines is their synthesis by the Pinner method (1877) [1], i.e. through the imino ethers. This method was used in our laboratory by A. N. Baksheev [2] to obtain linear amino acid amidines. These compounds are easily isolated from the reaction mixture as picrates. In the free state they are transformed into dark-colored, poorly crystallizing substances. Apparently, these linear amidines were also obtained by us in the decomposition of the condensation products of amino acid esters with Karrer's imino ether. We used the cyclic iminobenzyl ether, obtained by Karrer and Granacher from the silver salt of diketopiperazine and benzyl chloride [3]. The structure of this 2,5-dihydropyrazine O-O-dibenzyl ether was shown by both Karrer and by other investigators and remains undisputed [17, 19, 20]. It must be assumed that when reacted with amines it is transformed into a substituted amidine of the dihydropyrazine series.

With primary aliphatic and aromatic amines the reaction of amidine formation went with good yield, in which connection the A. N. Baksheev method [2] was used, and specifically, the reaction was run in the presence of picric acid. We failed to obtain the amino acid amidines, either by the direct reaction of amino acids and their esters with Karrer's ether or by the displacement of the formed aromatic or aliphatic amidine with amino acid esters. However, we failed to exhaust all of the possibilities for making the indicated reactions go in the desired direction. The literature on the conversion of imino ethers into amidines is reviewed in the monograph by Pinner [7] (see also [1, 2, 4, 7-18]).

From the studies of Baksheev, Drozdov and Bekhli [2, 4] and the earlier studies of Pinner it follows that in preparing the amidines from imino ethers the yields are greater in alcohol than they are in other solvents. Since the 2,5-dihydroxydihydropyrazine O,O-dibenzyl ether is soluble only in chloroform, we used a mixture of alcohol and chloroform as the reaction medium. Nevertheless, even under these conditions the reaction required a long time.

EXPERIMENTAL

1. Preparation of diphenyl-2,5-dihydropyrazineamidine dipicrate. The reaction mixture of 1 g O,O-dibenzyl-2,5-dihydroxydihydropyrazine, 0.63 g aniline, 1.5 g picric acid, 30 ml anhydrous methyl alcohol and 20 ml chloroform was agitated on a mechanical shaker for 2 weeks. The light brown transparent solution was concentrated in vacuum to low bulk without heating, and absolute ether was added to the residue. The yellow precipitate was washed repeatedly with ether until all of the picric acid had been removed. The diphenyl-2,5-dihydropyrazineamidine dipicrate obtained was readily soluble in acetone, alcohol, difficultly soluble in benzene and insoluble in ether. It melted at 193-193.5°. Yield 2.35 g (96%). This compound is not described in the literature.

Found %: C 46.84, 46.75; H 3.04, 3.06; N 19.13, 19.17. $C_{28}H_{22}O_{14}N_{10}$. Calculated %: C 46.54; H 3.06; N 19.38.

The dipicrate of the amidine of diphenyl-2,5-dihydropyrazine was converted to the corresponding dihydrochloride. 20 ml of absolute ether was added to 1 g of the dipicrate and a stream of dry hydrogen chloride was passed into the reaction mixture until it had a pH of 2-3. The precipitate was filtered off and washed a number of times with ether to remove the picric acid. It melted at 248-250° (decomp.). The dihydrochloride of diphenyl-2,5-dihydropyrazineamidine was soluble in methyl alcohol, dioxane and insoluble in acetone, benzene, ether and chloroform. It is not described in the literature.

Found %: C 57.26, 57.15; H 5.46, 5.54; N 16.83, 16.72. $C_{16}H_{18}N_4Cl_2$. Calculated %: C 56.98; H 5.31; N 16.61.

From the ethereal filtrate we isolated picric acid; m.p. 121° (122.5° according to the literature data).

Preparation of dipropyl-2,5-dihydropyrazineamidine dipicrate. It was prepared in the same manner as the preceding compound from 0.4 g O,O-dibenzyl-2,5-dihydroxydihydropyrazine, 0.16 g propylamine, 0.62 g picric acid, 10 ml methyl alcohol and 10 ml chloroform. It melted at 194-195°. The dipicrate of dipropyl-2,5-dihydropyrazineamidine was readily soluble in methyl alcohol; it was soluble in acetone, chloroform and insoluble in ether. Yield 0.8 g (98%). It is not described in the literature.

Found %: C 40.46, 40.59; H 4.16, 4.12; N 21.52, 21.77. $C_{22}H_{26}O_{14}N_{10}$. Calculated %: C 40.37; H 3.94; N 21.47.

By the above-described method we prepared the dihydrochloride of dipropyl-2,5-dihydropyrazineamidine. It melted at 204-206°. It was soluble in acetone, methyl alcohol and insoluble in ether and chloroform. It is not described in the literature.

Found %: N 20.90, 20.47. $C_{10}H_{22}N_4Cl_2$. Calculated %: N 20.80.

Reaction of O,O-dibenzyl-2,5-dihydropyrazine with benzylamine. When the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine was reacted with a molar quantity of benzylamine we obtained only the picrate of benzylamine.

We added 0.36 g benzylamine in 30 ml methyl alcohol and 0.77 g picric acid to 0.5 g O,O-dibenzyl-2,5-dihydroxydihydropyrazine in 20 ml of dry chloroform. The reaction mixture was agitated for about 2 weeks. The slightly colored solution was concentrated in vacuum to low bulk. The precipitate was filtered off and washed with ether; it melted at 193° (decomp.).

The literature data for the picrate of benzylamine give m.p. 195-199°.

Found %: N 16.50, 16.38 (Dumas). $C_{13}H_{12}O_7N_4$. Calculated %: N 16.60.

Ether was added to the concentrated filtrate. The precipitate which formed proved to be benzylamine picrate by its melting point range (189-192°) and its nitrogen content. From the picrate we prepared the hydrochloride, m.p. about 250°. The synthesized benzylamine hydrochloride melted at 246-250°.

Found %: N 9.59 (Dumas). $C_7H_{10}NCl$. Calculated %: N 9.74.

In the literature it is mentioned that the reaction of the imino ethers with amines proceeds better when the imino ethers possess greater tendency for ammonization than the amine component; therefore, the anomalous behavior of benzylamine in reaction with the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine can be explained by the strong tendency of benzylamine to ammonization. A similar phenomenon was observed by A. N. Baksheev [2] in the reaction of the imino ethers of α-amino acids with a molar quantity of benzylamine. The cited reactions in which amidines were formed took place only when 3-4 moles of benzylamine were used.

Reaction of O,O-dibenzyl-2,5-dihydroxydihydropyrazine with glycocoll. It was interesting to perform the coupling of O,O-dibenzyl ether with such a weakly ammoniated base as glycocoll. The success of this reaction would permit the synthesis of amidines of the dihydropyrazines of the amino acids themselves and not only of their esters. However, the experiment we performed for the condensation of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine with glycocoll in the presence of picric acid not only did not yield positive results but the presence of picric acid caused the decomposition of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine to glycocoll. The reaction resulted in isolating the picrate of glycocoll and the picrate of the methyl ester of glycocoll. It is worth noting that the esterification of glycocoll in the presence of such a weak acid as picric resulted in our obtaining the picrate of the methyl ester of glycocoll.

The reaction mixture of 1 g O,O-dibenzyl ether, 0.5 g glycocoll, 1.8 g picric acid, 30 ml of methyl alcohol and 15 ml chloroform was mechanically agitated for a month. The precipitate was washed with ether, acetone; it melted at 189°.

Found %: C 31.54, 31.64; H 3.54, 2.84; N 18.63, 18.51. $C_8H_8O_9N_4$. Calculated %: C 31.57; H 2.65; N 18.42.

The analytical data and the melting point of the isolated compound showed it to be the picrate of glycocoll (m.p. 190° [21]).

From 0.1 g of the picrate we prepared the hydrochloride. It melted at 182° (according to the literature data [22], its melting point is 184°).

Upon titration of the prepared hydrochloride (Willstätter), a weighed portion of 0.370 g consumed 6.6 ml of 0.1 N alcoholic NaOH which corresponded to 24.96% amino nitrogen. But since the hydrochloric acid as well as carboxyl were titrated with the alcoholic alkali, the amino nitrogen content was therefore 12.48%. This figure was in full agreement with the total nitrogen content determined in the same weighed-out portion.

Found %: N 12.50. $C_2H_6O_2NCl$. Calculated %: N 12.56.

The alcohol-chloroform filtrate from the precipitate was concentrated in vacuum to low bulk. The precipitate which came down was washed with ether, dissolved in a small quantity of alcohol and precipitated with ether. The prepared picrate of the methyl ester of glycocoll melted at 147°.

Found %: N 17.80, 17.48. $C_9H_{10}O_9N_4$. Calculated %: N 17.60.

From the picrate of the methyl ether of glycocoll, we isolated the hydrochloride of the methyl ester of glycocoll, m.p. 172° (the literature data gave m.p. 174° [23]).

Found %: N 11.2 (Willstätter). $C_3H_8O_2NCl$. Calculated %: N 11.15.

The literature [6] notes the possibility of the interchange of the groups present in the amidines. On the basis of this, we attempted to replace the phenyl group in the dipicrate of the amidine of diphenyl-2,5-dihydropyrazine with an amino acid residue.

0.3 g diphenyl-2,5-dihydropyrazineamidine dipicrate was mixed with 0.4 g of the methyl ester of tyrosine, 40 ml absolute ether was added to the mixture and the reaction mixture was stirred. After several minutes, a fluffy yellow precipitate came down. The mixture was stirred for several hours more. The precipitate was treated with methyl alcohol and the filtrate was settled with ether. The isolated compound was dried in a vacuum-desiccator. It melted at 182° (decomp.). It gave a positive anhydride reaction; the reaction for tyrosine was negative. The compound isolated proved to be diphenyl-2,5-dihydropyrazineamidine monopicrate.

Found %: C 53.45, 53.39; H 4.16, 4.23; N 19.83, 19.85. $C_{22}H_{19}O_7N_7$. Calculated %: C 53.55; H 3.85; N 19.87.

The compound, which was insoluble in methyl alcohol, gave a positive reaction for tyrosine; after treatment with warm benzene and drying in a vacuum-desiccator, it melted at 142° (decomp.); it proved to be the picrate of the methyl ester of tyrosine.

Found %: N 13.07, 12.92. $C_{16}H_{16}O_{10}N_4$. Calculated %: N 13.20.

From the ethereal filtrate from the initial precipitate, we isolated the initial methyl ester of tyrosine which was identified in the form of its hydrochloride; it melted at 184°. The synthesized hydrochloride of the methyl ester of tyrosine melted at 185°. A mixture test gave no depression.

The experiment performed showed that under the conditions chosen, only a redistribution of the picric acid occurred which resulted in the formation of diphenyl-2,5-dihydropyrazineamidine monopicrate and the picrate of the ester of tyrosine. However, this experiment did not exclude the possibility of performing the above reaction with the formation of the amidine of dihydropyrazine with an amino acid residue instead of a phenyl group. The success of the reaction of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine with amines encouraged us to attempt to prepare the corresponding amino-acid amidines by the indirect reaction of the O,O-dibenzyl ether of dihydropyrazine and the esters of amino acids. Our primary object of investigation was the hydrochloride of the ethyl ester of glycocoll.

Reaction of O,O-dibenzyl-2,5-dihydroxydihydropyrazine with the hydrochloride of the ethyl ester of glycocoll. a) At room temperature. The reaction mixture of 3 g O,O-dibenzyl-2,5-dihydroxydihydropyrazine, 2.85 g hydrochloride of the ethyl ester of glycocoll, 50 ml of chloroform and 30 ml anhydrous ethyl alcohol was mechanically agitated for a week. The colored solution was concentrated in vacuum, ether was added and the faintly colored precipitate that came down was filtered off. An attempt to remove the color by dissolving the precipitate in acetomethyl ether and by heating the solution with bone charcoal proved unsuccessful. The product was decolorized by repeatedly dissolving the precipitate in methyl alcohol and precipitating it with ether (half of the product was so treated); it gave a marked anhydride reaction and the ninhydrin and biuret reactions were negative.

Found %: NH_2 1.1 (Willstätter); N 15.57 (Kjeldahl). $C_{12}H_{20}O_4N_4$. Calculated %: NH_2 0.0; N 15.68.

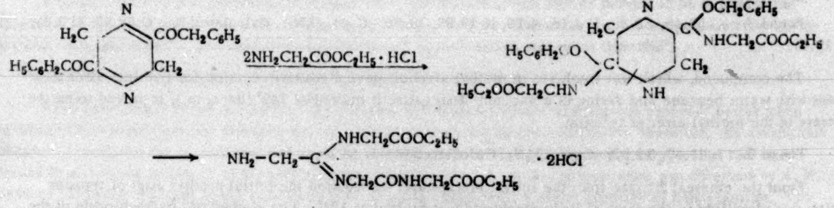
After repeated treatment of the compound with methyl alcohol and precipitation with ether, it decomposed into diketopiperazine and the hydrochloride of the ester of glycocoll. The properties of the product and analysis for nitrogen showed it to be probably the hydrochloride of the amidine of the diglycyldiethyl ether of dihydropyrazine.

b) With heating. To accelerate the reaction of the O,O-dibenzyl ether of dihydropyrazine and the hydrochloride of the ester of glycocoll, the reaction was performed at an elevated temperature and resulted in a product that darkened rapidly in air and deliquesced into a resinous mass.

When a solution of 2.5 g of the O,O-dibenzyl ether in chloroform was mixed with an alcoholic solution of 2.4 g of the hydrochloride of the ethyl ester of glycocoll, the initial substances precipitated out. The reaction mixture was heated at 50-70° for several hours and after only a half hour, the precipitate dissolved. When ether was added, a precipitate came down which was filtered off (carefully shielded from the moisture of the air), washed several times with ether and dried in a vacuum-desiccator.

Found %: C 38.85, 38.65; H 6.36, 6.23; N 16.03, 15.20. $C_{12}H_{24}O_5N_4Cl_2$. Calculated %: C 38.40; H 6.40; N 14.93.

Microscopic examination of the crystalline structure of the product showed that it differed from the usual amidine hydrochloride and probably was a tautomer in which hydrogen was absent at the nitrogen of the diketopiperazine. We could not perform biuret and anhydride tests due to the tendency of the product to color alkaline solutions a dark red. When the product was titrated (Willstätter) it further decomposed as indicated by the increased acidity of the solution as titration progressed. Judging from the properties of the product, it is difficult to assign it the structure of the usual dihydropyrazine amidine. It is probable that in the course of reaction of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine and the hydrochloride of the ethyl ester of glycocoll, the chain broke with the consequent formation of a linear amidine similar to that prepared by A. N. Baksheev.



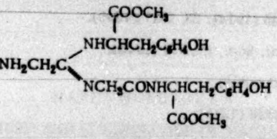
The work of A. N. Baksheev proved that the linear amidines of the amino acids with an unsubstituted amino group adjacent to the methylene group are noted for their slight stability in aqueous and alcoholic solutions, especially alkaline, which causes their initially colorless solutions to become colored.

The reaction took a similar course when the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine reacted with the methyl ester of tyrosine in the presence of picric acid.

Reaction of O,O-dibenzyl-2,5-dihydroxydihydropyrazine with the methyl ester of tyrosine. The reaction mixture of 0.5 g of O,O-dibenzyl ether, 0.66 g of the methyl ester of tyrosine, 0.77 g of picric acid, 30 ml anhydrous methyl alcohol and 20 ml of chloroform was mechanically agitated at room temperature for 2 weeks. The alcohol-chloroform solution was concentrated in vacuum and ether was added to the residue. The residue was washed repeatedly with ether, in absence of atmospheric moisture. The remaining solvent was removed in a vacuum-desiccator.

Found %: C 45.48, 45.59; H 3.83, 3.73; N 15.06, 14.98; NH_2 2.78, 3.05 (Van Slyke). $C_{36}H_{36}O_{21}N_{10}$. Calculated %: C 45.76; H 3.81; N 14.83; NH_2 2.72.

The picrate formed by the reaction rapidly converted to a dark greasy mass. Analysis and the amino nitrogen determination (according to Van Slyke) indicated the formation of a picrate of a linear amidine as a result of the decomposition of the initial addition product of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine and the methyl ester of tyrosine (by a reaction similar to the one mentioned in the previous section).



Reaction of O,O-dibenzyl-2,5-dihydroxydihydropyrazine with phthalylglycine acid chloride. In view of the fact that the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine behaves differently with respect to the amine group of amino acids and amines, it was decided to determine its ability to form N-substituted derivatives. With this purpose, the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine was reacted with phthalylglycine acid chloride and we obtained N,N'-diphthalylglycyldiketopiperazine, previously synthesized from diketopiperazine and phthalylglycine acid chloride.

1 g O,O-dibenzyldihydropyrazine was carefully mixed by trituration with 1.42 grams of phthalylglycine acid chloride. 20 ml xylene was added to the reaction mixture which was then heated on a water bath for 3 hours and 0.5 hour at the boiling point of the solvent (110°). The precipitate was filtered off and washed several times with alcohol and ether; the melting point of diphrhalylglycyldiketopiperazine was about 385° [6] (decomp.). It gave a positive anhydride reaction and a biuret reaction of the tripeptide type.

Found %: C 58.85, 58.79; H 3.46, 3.61; N 11.44, 11.46. $C_{24}H_{16}O_8N_4$. Calculated %: C 59.0; H 3.28; N 11.47.

SUMMARY

1. It was established that in the reaction of the O,O-dibenzyl ether of 2,5-dihydroxydihydropyrazine with amines the formation of amidine picrates of the dihydropyrazine series proceeds in nearly quantitative yield. Reaction of the latter with hydrogen chloride gave the corresponding amidine hydrochlorides. As a result we obtained: the diphenyl-2,5-dihydropyrazineamidine dipicrate, the diphenyl-2,5-dihydropyrazineamidine dihydrochloride, the di-2,5-dihydropyrazineamidine dipicrate and the dipropyl-2,5-dihydropyrazineamidine dihydrochloride, all of them previously unknown.

2. The reaction of O,O-dibenzyl-2,5-dihydroxydihydropyrazine with the esters of glycine and tyrosine gives linear polypeptide amidines. The formation of the latter is possible only as the result of asymmetric cleavage of the dihydropyrazine amino acid amidines obtained as intermediates in this reaction, which is also supported by the isolation (when glycine is used in the reaction) of diketopiperazine and the glycine ester.

3. An attempt to replace the phenyl groups in the amidine picrate of diphenyl-2,5-dihydropyrazine with the tyrosine radical for the purpose of obtaining an amino acid amidine proved unsuccessful.

4. The previously unknown diphenyl-2,5-dihydropyrazineamidine monopicrate was synthesized.

5. The reaction of the acid chloride of phthalylglycine with O,O-dibenzyldihydropyrazine gave N,N'-diphthalylglycyldiketopiperazine [6].

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NAPHTHOFUROXAN

V. SULFONATION AND CHLORINATION OF NAPHTHOFUROXAN

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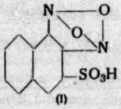
The structure of benzofurazan and benzofuroxan is usually depicted by ortho-quinoid formulas; in addition, the unsymmetrical structure of the furoxan ring is accepted for benzofuroxan. In the opinion of Hammick and coworkers [1], the proof for the quinoid structure of benzofuroxan and benzofurazan is the ability of these compounds to each add 4 atoms of bromine. The attempt of Gaughran and coworker [2] to obtain a symmetrical difuroxan, containing furoxan cycles in the 1,2 and 4,5-positions of the benzene ring, was unsuccessful. The authors considered this as confirmation of the quinoid structure for benzofuroxan.

In connection with the question of the structure of furoxan derivatives it appeared of interest to compare the behavior of 1,2-naphthofuroxan and 1,2-naphthofurazan in direct substitution reactions. As was mentioned earlier [3], in the sulfonation and chlorination of 1,2-naphthofurazan the substitution is mainly in the 3 position, i.e. it leads respectively to 1,2-naphthofurazan-3-sulfonic acid and 3-chloro-1,2-naphthofurazan. Nitration gives mainly the 5- and 7-nitro-1,2-naphthofurazans. The direct substitution of 1,2-naphthofuroxan has been studied but slightly. Its nitration by Green and Rowe [4] gave dinitro compounds (presumably 4,5-dinitro-1,2-naphthofuroxan).

We ran some experiments on the sulfonation and chlorination of 1,2-naphthofuroxan. Sulfonation with weak oleum at 20° gave a mixture of sulfonic acids, from which the 1,2-naphthofuroxan-3-sulfonic acid (I) was isolated in 53-60% yield. The chlorination of 1,2-naphthofuroxan with chlorine in sulfuric acid solution at 25° gave a mixture of reaction products, from which the 3-chloro-1,2-naphthofuroxan (II) was isolated in 30% yield.

The structure of the sulfonic acid was established by its conversion into 1,2-naphthylenediamine-3-sulfonic acid, and then into 1,2-naphthoselenodiazole-3-sulfonic acid (III), and comparing the latter with the analogous substance, obtained from 1-naphthylamine-3-sulfonic acid through 2-(4'-nitrophenylazo)-1-naphthylamine-3-sulfonic acid.

The structure of the chloronaphthofuroxan was shown by its comparison with the chloro derivative, obtained by the treatment of 1,2-naphthofuroxan-3-sulfonic acid with potassium hypochlorite and hydrochloric acid.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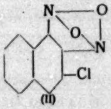
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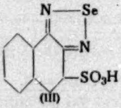
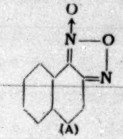
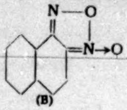

(III)

The similarity in the behavior of 1,2-naphthofuroxan and 1,2-naphthofurazan during sulfonation and chlorination supports the analogy in the structure of their naphthalene nucleii. Whereas for the unsubstituted benzofuroxan only one formula with an unsymmetrical structure for the furoxan cycle is possible, the structure of 1,2-naphthofuroxan can be depicted by two formulas: with an oxygen atom on the nitrogen, linked to the first carbon atom of the naphthalene cycle (A), and with an oxygen atom on the nitrogen, attached to the second carbon atom of the naphthalene ring (B).



(A)



(B)

The question as to the structure of 1,2-naphthofuroxan and its derivatives requires special study, for which reason a symmetrical structure was tentatively assumed for the furoxan ring in the formulas of 1,2-naphthofuroxan-3-sulfonic acid and 3-chloro-1,2-naphthofuroxan.

EXPERIMENTAL

1,2-Naphthofuroxan. It was prepared by the oxidation of the 1,2-naphthoquinone dioxime of nitric acid.

15.23 g unpurified naphthoquinone dioxime prepared from 0.09 mole of the sulfite compound of 1,2-naphthoquinone dioxime [5] was dissolved in 110 ml of 7.7% caustic potash. Into 150 ml 22.5% nitric acid, heated to 65-70°, the filtered solution was run in the course of 0.5 hour and the mixture was held at 90° for 15 minutes. The naphthofuroxan precipitate was filtered off and washed with water; the yield was 12.87 g (76.9%, on the sulfite compound of naphthoquinone dioxime), m.p. 121-123°. It was in the form of colorless needles (from alcohol); m.p. 124-125°.

1,2-Naphthofuroxan-3-sulfonic acid. 6.4 ml 62% fuming sulfuric acid was run in the course of 0.5 hour into a solution of 7.44 g of naphthofuroxan in 28 ml of the monohydrate at 20° and the mixture was held at the same temperature for 3 hours. The sulfo-mass was diluted with 500 g of ice, the warmed solution was neutralized with chalk and the gypsum was filtered off and washed with hot water. The calcium salt of the sulfonic acid which came down from the main filtrate was filtered off, dissolved in 300 ml of hot water and the calcium was precipitated with soda. Upon cooling the filtrate, 4.72 g of the sodium salt of the sulfonic acid separated out. The wash waters from the gypsum together with the filtrate from the calcium salt were evaporated down and the calcium was precipitated with soda. Upon evaporating down the obtained solution of the sodium salt and the filtrate from the precipitated sodium salt to 100 ml, 1.8 g more of the sodium salt of the sulfonic acid separated out; total yield 6.52 g (53.2%). On further evaporation a non-crystallizable gelatinous mass formed.

Upon repetition of the experiments using 7.44, 3.72 and 28.86 g of naphthofuroxan, we obtained correspondingly 6.7, 3.7 and 26.4 g of the sodium salt of the sulfonic acid (54.7, 60.4 and 55.6% correspondingly).

The sodium salt was in the form of colorless platelets (from water), quite difficulty soluble in water and alcohol.

Found %: H_2O 6.17; Na 7.94. $C_{10}H_5O_5N_2SNa \cdot H_2O$. Calc: %: H_2O 5.89. $C_{10}H_5O_5N_2SNa$. Calculated %: Na 7.98.

The sulfochloride was in the form of colorless prisms (from carbon tetrachloride), difficulty soluble in benzene, chlorobenzene, carbon tetrachloride and dichloroethane; m.p. 221° (decomp.).

Found %: N 9.71; Cl 12.36. $C_{10}H_5O_4N_2SCl$. Calculated %: N 9.84; Cl 12.46.

1,2-Naphthoselenodiazole-3-sulfonic acid. a) From 1,2-naphthofuroxan-3-sulfonic acid. The reduction of 1,2-naphthofuroxan-3-sulfonic acid was performed the same as the reduction of 1,2-naphthofuroxan-4-sulfonic acid with zinc dust and hydrochloric acid in the presence of stannous chloride [6]. From 7.7 g of the sodium salt of the sulfonic acid we obtained 3.8 g of 1,2-naphthylenediamine-3-sulfonic acid (long colorless needles).

1,2-Naphthoselenodiazole-3-sulfonic acid was prepared by the action of selenium dioxide on 1,2-naphthylenediamine-3-sulfonic acid as described for the case of 1,2-naphthoseleneodiazole-4-sulfonic acid [7]. From 4.04 g of the diamino compound we obtained 5.8 g of the sodium salt of naphthoselenodiazolesulfonic acid.

The sodium salt was in the form of colorless prisms (from water), fairly readily soluble in water and insoluble in alcohol; it colored yellow from methyl alcohol.

Found %: H_2O 9.59; Na 6.78. $C_{10}H_5O_3N_2SeSNa \cdot 2H_2O$. Calculated %: H_2O 9.70. $C_{10}H_5O_3N_2SeSNa$. Calculated %: Na 6.86.

The sulfochloride was in the form of colorless prisms (from chlorobenzene); m.p. 230° (decomp.).

b) From 2-(4'-nitrophenylazo)-1-naphthylamine-3-sulfonic acid. The azo compound was prepared by coupling 1-naphthylamine-3-sulfonic acid with p-nitrodiazobenzene [8]. Cleavage of the azo compound was performed with zinc dust in a 4% solution of sodium chloride in the presence of copper sulfate [9]; 1,2-naphthylenediamine-3-sulfonic acid was reprecipitated from sulfite-soda solution.

The sodium salt of naphthoselenodiazolesulfonic acid was in the form of colorless prisms (from water).

Found %: H_2O 9.79; Na (in the dry substance) 6.81.

The sulfochloride was in the form of colorless prisms (from chlorobenzene); m.p. 229.5° (decomp.). The mixture of the sulfochlorides melted at 229.5° (decomp.).

3-Chloro-1,2-naphthofuroxan. a) From 1,2-naphthofuroxan. Chlorine was passed into a solution of 23.3 g of naphthofuroxan in 200 ml of 95.5% sulfuric acid at 25° in the course of 2 hours until a 4.4 g weight addition. The reaction mass was poured on ice, the precipitated chloroderivative was filtered off and washed with water, alcohol and ether; the yield was 27.3 g, melting range 114-128°, and after 4 crystallizations from carbon tetrachloride, the yield of the compound was 8.5 g (30.8%); m.p. 145.5-146.5°.

It was in the form of colorless needles (from carbon tetrachloride), readily soluble in acetic acid, acetone and carbon tetrachloride, and difficulty soluble in ether.

Found %: C 54.44; H 2.02; Cl 16.14. $C_{10}H_5O_2N_2Cl$. Calculated %: C 54.44; H 2.28; Cl 16.07.

b) From 1,2-naphthfuroxan-3-sulfonic acid. A solution of 7.35 g calcium chlorate in 100 ml of water was run into a boiling solution of 6.12 g of the sodium salt of naphthofuroxansulfonic acid in 350 ml of 3.3% hydrochloric acid in the course of 3 hours, and boiling was continued for 1 hour more. Upon cooling, the chloro derivative was filtered off and washed with water; its yield was 1.5 g, melting range 139-143°. It was in the form of colorless needles (from carbon tetrachloride), m.p. 145.5-146.2°.

Found %: C 54.48; H 2.05; Cl 15.85.

The mixture of the chloro derivatives melted at 145.5-146.2°.

SUMMARY

1. 1,2-Naphthofuroxan-3-sulfonic acid was isolated from the products obtained in the sulfonation of 1,2-naphthofuroxan with weak oleum at 20°.

2. 3-Chloro-1,2-naphthofuroxan was isolated from the products obtained in the chlorination of 1,2-naphthofuroxan with chlorine in sulfuric acid and from the products obtained in the chlorination of 1,2-naphthofuroxan-3-sulfonic acid with potassium hypochlorite in hydrochloric acid.

3. The direction of substitution in the chlorination and sulfonation of 1,2-naphthofuroxan supports the opinion that the structures of the naphthalene nuclei in 1,2-naphthofuroxan and 1,2-naphthofurazan are the same.

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SYNTHESIS OF TRIALKYLSILANEPHOSPHORIC ACIDS

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Organic silicophosphorus compounds have received but slight illumination in the literature, despite the fact that they represent definite interest both in theory and in practice. The diethyl ester of triethylphosphonosilane, prepared by the reaction of triethyl bromosilane with triethyl phosphite, has been described in the literature [1]. Later, in studying a similar reaction [2], it was postulated that a compound having the formula $(C_2H_5)_3SiP(=O)[OSi(C_2H_5)_3]OC_2H_5$ was formed.

The aromatic silicon-containing phosphorus derivatives: tris(p-trimethylsilylphenyl)phosphine, bis(p-trimethylsilylphenyl)chlorophosphine, tris(p-trimethylsilylphenyl)phosphine oxide and bis(p-trimethylsilylphenyl)phosphinic acid – were isolated in the reaction of p-trimethylsilylphenylmagnesium bromide with phosphorus tri- or pentachloride [3].

Chemical reaction occurs in the condensation of polydiethylsiloxanes with P_2O_5 to give complex organic silicophosphorus compounds [4].

Phosphorus compounds are used as additives in the preparation of polydimethylsiloxane elastomers [5] and various organosilicon resins [6]. Up to now there fail to exist in the literature any definite statements on the preparation of monomeric organosilicon compounds having the $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{P}}=$ bond.

In studying the reaction of trialkylchlorosilanes with potassium dihydrogen phosphate we established [7] that trialkylsilanephosphoric acids are formed by the following scheme as a result of this process:

$$R_3SiCl + KH_2PO_4 \rightleftharpoons R_3SiOPO(OH)_2 + KCl.$$

This reaction proceeds in diethyl ether medium in 80-90% yield, and in either benzene or xylene medium in 11-12% yield.

Of the trialkylchlorosilanes we took trimethylchlorosilane and triethylchlorosilane. When reacted we obtained here trimethylsilanephosphoric acid, being colorless crystals with m.p. 66.0-66.5°, and triethylsilanephosphoric acid – a viscous, pale yellow liquid, failing to distill in vacuo and decomposing when heated above 200°.

It was experimentally shown that the obtained compounds are easily hydrolyzed by water to give the hexaalkyldisiloxane and phosphoric acid:

$$2R_3SiOPO(OH)_2 + H_2O \rightarrow R_3SiOSiR_3 + 2H_3PO_4.$$

EXPERIMENTAL

Trimethylsilanephosphoric acid. 162.9 g (1.5 mole) trimethylchlorosilane (b.p. 56-58°, chlorine content 34.1%) and 204.2 g (1.5 mole) potassium dihydrogen phosphate and solvent amounting to 100% of the weight of chloride were placed in a 3-necked flask fitted with oil sealed stirrer, thermometer and condenser with calcium chloride tube. The reaction was performed at 20-22° with stirring for 5 hours. After the inorganic precipitate was separated off, the filtrate was driven off in vacuum at a residual pressure of 1-2 mm. After the solvent was driven off with unreacted trimethylchlorosilane, the residue was in the form of a viscous liquid which crystallized upon standing. After recrystallization from benzene, we isolated pure crystals of trimethylsilanephosphoric acid, m.p. 66.0-66.5°.

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* Deceased.

Found %: Si 16.2; P 18.5; OH 21.69. $C_3H_{11}O_4SiP$. Calculated %: Si 16.4; P 18.05; OH 19.80.

Triethylsilanephosphoric acid was synthesized by the same scheme from 225.8 g (1.5 mole) triethylchlorosilane (b.p. 143-144°, chlorine content 23.55%) and 204.2 g (1.5 mole) potassium dihydrogen phosphate. The reaction yielded a viscous liquid of a straw-yellow color. Upon long standing at room temperature and also cooling or heating, it did not crystallize. The liquid, triethylsilanephosphoric acid, was non-distilling and decomposed above 200°.

Found %: Si 13.72; P 15.1; OH 16.87. $C_6H_{17}B_4SiP$. Calculated %: Si 13.20; P 14.5; OH 16.05.

Hydrolysis of trimethylsilanephosphoric acid. 5 g trimethylsilanephosphoric acid in 10 g of water was placed in a separating funnel with ground stopper. The mixture was well stirred for 10-20 minutes manually and after standing, the organic and aqueous layers were carefully separated and weighed. The aqueous layer contained phosphorus and did not contain silicon, and the organic layer contained silicon and did not contain phosphorus.

The organic layer was dried over Na_2SO_4 and distilled at atmospheric pressure. Distillation yielded pure hexamethyldisiloxane, m.p. 100° and n_D^{23} 1.3742.

The literature data for hexamethyldisiloxane [8]: b.p. 100°, n_D^{25} 1.3748, n_D^{20} 1.3722.

Found %: Si 34.5. $C_6H_{18}OSi_2$. Calculated %: Si 34.6.

Hydrolysis of triethylsilanephosphoric acid was performed the same as hydrolysis of trimethylsilanephosphoric acid.

Our product was hexaethyldisiloxane, b.p. 229-232° and n_D^{23} 1.4344.

Literature data for hexaethyldisiloxane [8]: b.p. 231°, n_D^{20} 1.4340.

Found %: Si 20.3. $C_{12}H_{30}OSi_2$. Calculated %: Si 22.76.

Analysis of the prepared compounds was as follows: a weighed portion of the compound (about 0.2 g) was dissolved in concentrated sulfuric acid and KIO_3 was added to the solution so obtained, the solution was evaporated down until the evolution of iodine fumes stopped, the residue was then diluted with water, silicon dioxide was filtered off, calcined and weighed. In order to determine the phosphorus, a weighed portion of the compound was dissolved in a mixture of concentrated sulfuric and nitric acids. The solution was diluted with water, the SiO_2 precipitate was filtered off and the phosphorus was determined in the filtrate by 2-fold precipitation.

SUMMARY

A number of trialkylsilanephosphoric acids were synthesized and it was shown that they are easily hydrolyzed with water to give hexaalkyldisiloxanes and phosphoric acid.

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ALKOXYDIANILIDOPHOSPHAZOSULFONARYLS

V. I. Shevchenko and V. V. Bondarev

The chlorodianilidophosphazosulfonaryls (the chlorides of the dianilides of arylsulfonimidophosphoric acids), obtained in good yields from trichlorophosphazosulfonaryls and aniline [1], show ready reaction with either sodium methylate or ethylate to give alkoxydianilidophosphazosulfonaryls, in accord with the scheme:

$$ArSO_2N=PCl(NHC_6H_5)_2 \xrightarrow{AlkONa} ArSO_2N=P(OAlk)(NHC_6H_5)_2.$$

The alkoxydianilidophosphazosulfonaryls are colorless crystalline substances (tiny prisms). They are all soluble in water, ether and petroleum ether, quite readily soluble in boiling alcohol and acetone, and more difficulty soluble in hot benzene and carbon tetrachloride. Chemically the alkoxydianilidophosphazosulfonaryls are stable and neutral, and fail to react with water under prolonged heating. They are also stable to dilute mineral acids. When heated at the boil for 1 hour with 0.2 N aqueous-alcohol hydrochloric acid solution the alkoxydianilidophosphazosulfonaryls fail to be changed. They are less stable to alkalies and are quite easily saponified with 0.2 N aqueous-alcohol sodium hydroxide solution to give the sodium salts of the arylsulfonamidophosphoric acid dianilides.

We were unsuccessful in our attempt to prepare the methoxydianilidophosphazosulfonaryls from the methoxydichlorophosphazosulfonaryls [2] and aniline. Here we obtained oily viscous substances that failed to crystallize.

The previously unknown chlorodianilidophosphazosulfon-β-naphthyl was obtained by the method described in the literature [1].

The formulas, yields, melting points and alkoxyl contents of the obtained alkoxydianilidophosphazosulfonaryls are given in the table.

EXPERIMENTAL

Preparation of methoxy- and ethoxydianilidophosphazosulfonaryls. 0.003 mole of metallic sodium was dissolved in 10 ml of anhydrous methyl or ethyl alcohol. 0.003 mole of powdered chlorodianilidophosphazosulfonaryl was then added to the above solution. The reaction evolved a considerable amount of heat. The chloride dissolved and a precipitate of the alkoxy compound immediately came down. After an hour, 10 ml of water was added to the reaction mixture. The precipitate of alkoxydianilidophosphazosulfonaryl was sucked off, washed with water and dried. The yield was 85-95%. The product was purified by crystallization from dilute alcohol (prisms).

Hydrolysis of methoxy- and ethoxydianilidophosphazosulfonphenyl with alcoholic caustic soda solution. 12.5 ml of aqueous alcoholic caustic soda solution (2.5 ml of 1 N caustic soda solution +10 ml of alcohol) was run into 0.005 mole of alkoxydianilidophosphazosulfonphenyl. The mixture was heated on a water bath for an hour and the excess alcohol was then driven off in vacuum and 10 ml of water was added to the residue. The unhydrolyzed ether was sucked off, washed with water, dried and weighed. The filtrate which contained the sodium salt of the dianilide of phenylsulfonamidophosphoric acid was acidified with concentrated hydrochloric acid until it gave an acid reaction with congo. The dianilide which came down was separated and washed with a small amount of H_2O. From the methoxydianilidophosphazosulfonphenyl we obtained 0.17 g (87.5%) of the dianilide of phenylsulfonamidophosphoric acid, from the

TABLE

Formula	Yield (%)	Melting point (°C)	Found alkoxyl content (%)	Empirical formula	Calculated alkoxyl content (%)
$C_6H_5SO_2N=P(OCH_3)(NHC_6H_5)_2$	83.3	197-198°	7.57	$C_{19}H_{20}O_3PSN_3$	7.73
o-$CH_3C_6H_4SO_2N=P(OCH_3)(NHC_6H_5)_2$	93.9	136-137	7.62	$C_{20}H_{22}O_3PSN_3$	7.47
p-$CH_3C_6H_4SO_2N=P(OCH_3)(NHC_6H_5)_2$	96.3	150-151	7.38	$C_{20}H_{22}O_3PSN_3$	7.47
α-$C_{10}H_7SO_2N=P(OCH_3)(NHC_6H_5)_2$	90.8	159-161	6.66	$C_{23}H_{22}O_3PSN_3$	6.87
β-$C_{10}H_7SO_2N=P(OCH_3)(NHC_6H_5)_2$	95.2	188-191	6.84	$C_{23}H_{22}O_3PSN_3$	6.87
$C_6H_5SO_2N=P(OC_2H_5)(NHC_6H_5)_2$	96.3	178-179	10.72	$C_{20}H_{22}O_3PSN_3$	10.85
o-$CH_3C_6H_4SO_2N=P(OC_2H_5)(NHC_6H_5)_2$	81.5	113-114.5	10.34	$C_{21}H_{24}O_3PSN_3$	10.49
p-$CH_3C_6H_4SO_2N=P(OC_2H_5)(NHC_6H_5)_2$	86.1	148-149	10.54	$C_{21}H_{24}O_3PSN_3$	10.49
α-$C_{10}H_7SO_2N=P(OC_2H_5)(NHC_6H_5)_2$	95.9	156-158	9.88	$C_{24}H_{24}O_3PSN_3$	9.68
β-$C_{10}H_7SO_2N=P(OC_2H_5)(NHC_6H_5)_2$	87.1	166-167	9.72	$C_{24}H_{24}O_3PSN_3$	9.68

ethoxy compound we obtained 0.08 g (41.3%) or the corresponding dianilide and 0.09 g (43.3%) of unhydrolyzed product which returned. The hydrolysis products were identified by melting point and titration data [1].

Preparation of Chlorodianilidophosphazosulfon-β-naphthyl. 0.02 mole (6.85 g) of trichlorophosphazosulfon-β-naphthyl was dissolved with heating in 50 ml of dry carbon tetrachloride. The solution was rapidly cooled. A solution of 0.08 mole (7.45 g) of aniline in 25 ml of carbon tetrachloride was added with stirring and cooling to the fine crystals which came down. The mixture was set aside for a day. The precipitate which came down was separated off and extracted 3 times with 100 ml of boiling benzene. Upon cooling, crystals came down which were separated off and recrystallized from benzene (fine needles). The yield was 3.2 g (35.4%), m.p. 124-125°. The product was readily soluble in acetone, alcohol and relatively well in hot benzene, difficulty – in carbon tetrachloride and in ether.

Found equiv. of acid after hydrolysis 1.97. $C_{22}H_{19}O_2PSN_3Cl$. Calculated equiv. of acid after hydrolysis 2.00.

Preparation of dianilido-β-naphthylsulfonimidophosphoric acid. 0.005 mole chlorodianilidophosphazosulfone-β-naphthyl (0.26 g) ground to a fine powder, was mixed with 2 ml of water and to this suspension was added 0.2 N caustic soda solution until an alkaline reaction was obtained with phenolphthalein. The solution was then acidified with hydrochloric acid until it gave an acid reaction with Congo, and the dianilide of β-naphthylsulfonamidiphosphoric acid which came down was separated off, washed and dried. The yield was 0.20 g (81.5%). After recrystallization from aqueous alcohol it had m.p. 210-211°.

Found equiv. of acid 1.008. $C_{22}H_{20}O_3PSN_3$. Calculated equiv. of acid 1.000.

SUMMARY

The methoxy- and ethoxydianilidophosphazosulfonaryls were obtained and their properties were described.

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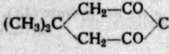
2-NITRO-PERINAPHTH-1,3-INDANDIONE AND SOME OF ITS DERIVATIVES

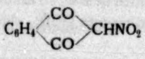
E. Yu. Gudrinietse, E. Ya. Dreimanis and G. Ya. Vanag

Some of us [1] had recently described nitrodimedon or 4-nitro-1,1-dimethyl-1,3-cyclohexanedione (I), which reacts as an acid in aqueous solutions and readily forms salts. Nitrodimedon, similar to the systematically studied 2-nitro-1,3-indandione (II), readily enters into condensation reactions. The obtained products can also possess practical utility [2]. In connection with this it appeared of interest to also study the properties of other cyclic nitro-β-diketones. For this purpose we prepared the previously unknown 2-nitro-perinaphth-1,3-indandione (IV). Perinaphthindandione (III) itself was prepared by the Errera method [3], which we modified somewhat and made shorter.



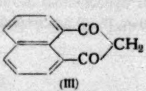
$$(CH_3)_2C\begin{matrix}CH_2-CO\\CH_2-CO\end{matrix}CHNO_2$$

(I)



$$C_6H_4\begin{matrix}CO\\CO\end{matrix}CHNO_2$$

(II)



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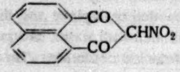

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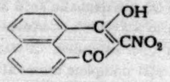

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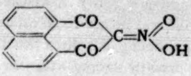


(VI)

Nitration of the perinaphthindandione with concentrated nitric acid in glacial acetic acid gave 2-nitro-perinaphth-1,3-indandione in about 65% yield. This yellow crystalline substance melts at 160°. Difficultly soluble in water, readily soluble in ethyl alcohol and in glacial acetic acid, and insoluble in ether and benzene; it readily dissolves in caustic alkalies and in ammonia to form salts.

Nitro-perinaphthindandione, the same as nitroindandione and nitrodimedon, can exist in several tautomeric forms (IV, V and VI). It still has not been determined which of these forms are involved in the formation of salts.

Since 2-nitro-perinaphth-1,3-indandione itself is but slightly soluble in water (1:4000), its salts were usually prepared from the soluble sodium salt by the exchange method. The sodium salt was also used for the precipitation of organic bases from their aqueous salt solutions. The salts of nitroperinaphthindandione with organic bases can also be obtained directly from the nitro-perinaphthindandione itself in alcohol solution, but frequently the resulting salts are readily soluble in alcohol and fail to give a precipitate. In general, the salts of nitro-perinaphthindandione with organic bases proved to be even less soluble in water than the corresponding nitro-indandione salts.

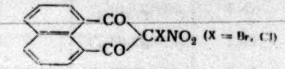
Of the inorganic salts of nitro-perinaphthindandione the divalent iron salt, which is also characteristic for nitro-indandione [4] and for nitrodimedon [1], was of especial interest to us. It was found that here also the divalent iron salt of the nitro-perinaphthindandione differs sharply from the other salts. All of the nitro-perinaphthindandione salts are mainly yellow, but the divalent iron salt is almost black. It crystallizes with 4 molecules of water, the same as the corresponding nitroindandione salt. The approximate solubility of some of the nitro-perinaphthindandione salts can be seen from the table.

TABLE

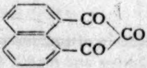
Limiting Dilution of Salt Solutions at Which a Precipitate is Still Obtained With a Saturated Solution of the Nitro-perinaphthindandione Sodium Salt

Salt	Solution dilution	Solution normality
$Pb(NO_3)_2$	1:6000	0.001
$BaCl_2$	1:48000	0.0002
$SrCl_2$	1:62000	0.0002
$FeSO_4$	1:13000	0.001
Aniline (in dilute acetic acid	1:10000	0.001
o-Toluidine (in dilute acetic acid)	1:2800	0.003
m-Toluidine (in dilute acetic acid)	1:1900	0.005
p-Toluidine (in dilute acetic acid)	1:4700	0.002

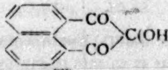
Nitro-perinaphthindandione, the same as nitrodimedon and nitroindandione, is easily brominated and chlorinated, forming the corresponding bromo- and chloro derivatives (VII):



(VII)



(VIII)



(IX)

The halonitro-perinaphthindandiones are soluble in alcohol, gasoline, chloroform and carbon tetrachloride, and are slightly soluble in ether. When boiled with water these compounds decompose with the cleavage of either hypochlorous or hypobromous acid. When heated in nitrobenzene, the bromonitro-perinaphthindandione forms the already known [5, 6] perinaphthindantrione (VIII), which easily gives the hydrate (IX).

EXPERIMENTAL

Perinaphthindandione-1,3 (III). A mixture of 30 g naphthalic acid anhydride, 60 g malonic ester and 30 g anhydrous zinc chloride was heated in an oil bath to 170-175°. A violet reaction took place and the mixture colored yellow. Upon cooling, the thick reaction mass solidified. It was diluted with water, the precipitate was filtered off and carefully washed with water until complete removal of the zinc chloride. The residue was dissolved in caustic soda, filtered and acidified. The precipitate which came down was perinaphthindandione-1,3. After crystallization from a mixture of ethyl alcohol and glacial acetic acid (1:1), we isolated 20 g of completely pure product which corresponded to the literature data.

2-Nitro-perinaphthindandione-1,3 (IV). A mixture of 8 g of perinaphth-1,3-indandione, 80 ml of glacial acetic acid and 20 ml of nitric acid (d 1.365) was heated on a water bath until the perinaphthindandione dissolved. Upon rapid cooling with cold water, yellow crystals of 2-nitro-perinaph-1,3-indandione came down. The crystals were separated off, washed with acetic acid, recrystallized from ethyl alcohol. The yield was 6.4 g (65%) of yellow acicular crystals, m.p. 160°.

Found %: N 5.86. $C_{13}H_7O_4N$. Calculated %: N 5.81.

Salts of 2-nitro-perinaphth-1,3-indandione. Sodium Salt. 2-Nitroperinaphth-1,3-indandione was heated with a solution of caustic soda and filtered. Upon cooling, yellow crystals of the sodium salt of nitroperinaphthindandione came down from the solution.

Alcoholic caustic soda solution was added to an alcoholic solution of 2-nitro-perinaphth-1,3-indandione. The solution congealed into a yellow mass. The precipitate was filtered off, washed with alcohol and recrystallized from water. It was soluble in water to the extent of 1:200 parts, less – in alcohol. Upon heating, the salt decomposed without melting.

Found %: N 5.14. $C_{13}H_6O_4NNa$. Calculated %: N 5.32.

Potassium salt. It was prepared in the same manner as the sodium salt. It was in the form of yellow needles. It was soluble in water, difficulty – in alcohol.

Found %: N 4.92. $C_{13}H_6O_4NK$. Calculated %: N 5.02.

Ammonium salt. Concentrated ammonia was poured over 2-nitro-perinaphthindandione and the mixture was boiled until complete solution of the solid. Upon cooling the ammonium salt of nitro-perinaphthindandione, containing 3 molecules of water, precipitated out.

Found %: N 9.02. $C_{13}H_6O_4NNH_4 \cdot 3H_2O$. Calculated %: N 8.97.

Upon drying at 50-60° (to constant weight) the salt lost 1 molecule of water.

Found %: N 9.43. $C_{13}H_6O_4NNH_4 \cdot 2H_2O$. Calculated %: N 9.52.

Upon drying at 110-120° (to constant weight) the salt lost 1 more molecule of water.

Found %: N 9.82. $C_{13}H_6O_4NNH_4 \cdot H_2O$. Calculated %: N 10.14.

The last molecule of water could not be removed since above 120°, the compound decomposed with evolution of ammonia

Lead salt. It was prepared by the addition of lead nitrate solution to an aqueous solution of the sodium salt of nitro-perinaphthindandione. It was in the form of yellow platelets, difficulty soluble in water.

Found %: N 3.79; Pb 29.95. $(C_{13}H_6O_4N)_2Pb$. Calculated %: N 4.07;
Pb 30.13.

Barium salt. It was prepared in the same manner as the lead salt. It was in the form of yellow platelets.

Found %: N 4.35. $(C_{13}H_6O_4N)_2Ba$. Calculated %: N 4.54.

Strontium salt. It was prepared in the same manner as the lead salt. It was in the form of light yellow needles.

Found %: N 4.71. $(C_{13}H_6O_4N)_2Sr$. Calculated %: N 4.93.

Ferrous salt. It was prepared from Mohr's salt and nitro-perinaphthindandione in aqueous solution in the presence of acetic acid. It was in the form of dark, almost black needles. It crystallized with 4 molecules of water which it lost at 75°.

Found %: N 4.63; H_2O 11.89. $(C_{13}H_6O_4N)_2Fe \cdot 4H_2O$. Calculated %: N 4.61;
H_2O 11.84.

Aniline salt. An ethereal solution of aniline was added to the alcoholic solution of nitro-perinaphthindandione. Yellow platelets of the aniline salt of nitro-perinaphthindandione precipitated out. After crystallization from alcohol, the salt melted at 179-180° (with decomp.).

The salt also could be prepared by precipitation of an aqueous solution of the aniline salt by the sodium salt of nitro-perinaphthindandione or by solution of aniline in acetic acid and precipitation of a solution of the sodium salt of nitro-perinaphthindandione.

Found %: N 8.12. $C_{19}H_{14}O_4N_2$. Calculated %: N. 8.38.

The toluidine salts were prepared in the same manner. They were in the form of yellow crystals from alcohol. The o-toluidine salt melted at 189-190° and the m-toluidine salt – at 192-193°.

For the ortho- and meta-salts:

Found %: N 8.10, 7.95. $C_{20}H_{16}O_4N_2$. Calculated %: N 8.05.

2-Bromo-2-nitro-perinaphth-1,3-indandione(VII, X = Br). 0.5 g of the sodium salt of nitro-perinaphthindandione was dissolved in 100 ml of water and an excess of bromine water was added to the solution. The precipitate was filtered off, washed with water and recrystallized from alcohol. It was in the form of colorless needles. Upon standing in the air, it colored yellow and bromine was given off. At 165°, the compound colored red and melted at 230-235°. Evidently, at this point perinaphthindandione formed which was also formed upon boiling 2-bromo-2-nitro-perinaphthindandione in nitrobenzene.

Found %: N 4.46. $C_{13}H_6O_4NBr$. Calculated %: N 4.38.

Naphthindantrione (VIII) and its hydrate (IX). 1 ml of nitrobenzene was poured over 1 g of bromo-nitro-perinaphthindandione and the mixture was heated to the boiling point. The substance dissolved and the liquid colored red and brown fumes were given off (nitrosyl bromide). Upon cooling, a red precipitate of naphthindantrione came down which was separated off and washed with benzene. The yield was 0.5 g. After crystallization from 25 ml of very dilute acetic acid, we isolated 0.25 g of yellow crystals of perinaphthindantrione hydrate, corresponding to the compound described in the literature. Upon heating to 100°, the hydrate lost water and was again converted to the red naphthindantrione. In concentrated soda solution it dissolved giving a blue coloration and with α-amino acids it gave a red coloration.

SUMMARY

1. A simplified method was developed for the preparation of perinaphthindandione.

2. The nitration of perinaphthindandione gave 2-nitro-perinaphth-1,3-indandione, the properties of which were studied and a number of its inorganic and organic salts were prepared.

3. The treatment of the sodium salt of 2-nitro-perinaphth-1,3-indandione with Br gave 2-bromo-2-nitroperinaphth-1,3-indandione. When heated in nitrobenzene it is converted into the perinaphthindantrione.

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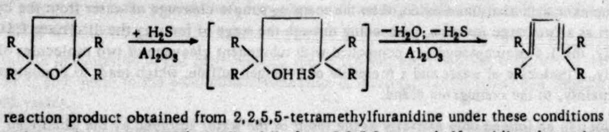
CATALYTIC TRANSFORMATIONS OF HETEROCYCLIC COMPOUNDS

XLVII. MECHANISM OF THE CATALYTIC DEHYDRATION OF 2,2,5,5-TETRAMETHYLFURANIDINE

Yu. K. Yuryev and G. Ya. Kondratyeva

In our previous studies on the catalytic transformation of furanidine (tetrahydrofuran) homologs into thiophane homologs it was established that the structure of the starting oxygen-containing heterocycle exerts great influence on the course of this reaction [1].

Among furanidine homologs the 2,2,5,5-tetraalkylfuranidines occupy a special place, and when treated with hydrogen sulfide in the presence of aluminum oxide proved incapable of replacing the oxygen bridge by sulfur and gave only unsaturated hydrocarbons; the latter, as we postulate, were formed as the result of both water and hydrogen sulfide being cleaved from the 1,4-mercaptohydroxy compound, intermediately formed as the result of ring opening under the influence of hydrogen sulfide:



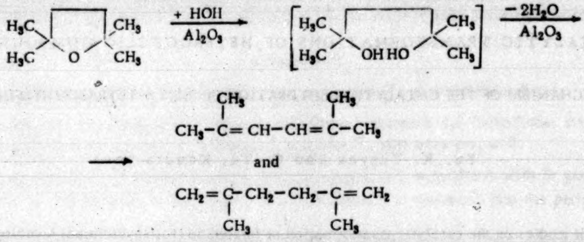
The main reaction product obtained from 2,2,5,5-tetramethylfuranidine under these conditions was 2,5-dimethyl-2,4-hexadiene (diisocrotyl) (30% yield), while from 2,2,5,5-tetraethylfuranidine the main reaction product was 3,6-diethyl-3,5-octadiene (27.5% yield) [2].

There is no doubt but that the reaction proceeds through the above indicated intermediate stage of forming the 1,4-mercaptohydroxy compound and fails to reduce to a simple cleavage of water from the cyclic oxide as such, since both the nature of the formed hydrocarbons and their yield are very greatly dependent on the presence of hydrogen sulfide.

A comparison of the results, obtained when 2,2,5,5-tetramethylfuranidine was passed over aluminum oxide in the presence of hydrogen sulfide and in its absence, reveals that in a hydrogen sulfide atmosphere the reaction is more unidirectional and leads to a more homogeneous end product — mainly to the diene hydrocarbon with a conjugated system of double bonds.

In the absence of hydrogen sulfide the dehydration of 2,2,5,5-tetramethylfuranidine fails to obey any simple rule, and the reaction product is a mixture of hydrocarbons, the composition of which can be established only by using the method of repeated distillations through an efficient fractionation column and the Raman spectra method to study the narrow fractions isolated in the distillations. To this should be added the fact that the compounds, which appeared as the main transformation products when the reaction was run in a hydrogen sulfide atmosphere and therefore could be easily isolated, in the absence of hydrogen sulfide were obtained in small amount and indirectly [3].

The dehydration of 2,2,5,5-tetramethylfuranidine over aluminum oxide at 350° in a water-vapor atmosphere, described by us in this communication, in its results proved to be extremely close to the reaction proceeding in a hydrogen sulfide atmosphere [2]. Here also the main reaction product is 2,5-dimethyl-2,4-hexadiene (diisocrotyl), which was obtained in 50% yield, while the 2,5-dimethyl-1,5-hexadiene (diisobutenyl) was obtained in smaller amount, in an 18% yield. The high yield of diunsaturated hydrocarbons and especially of diisocrotyl shows that the catalytic dehydration of 2,2,5,5-tetramethylfuranidine in the presence of water vapors proceeds as uniformly as in a hydrogen sulfide atmosphere and is accomplished by the same mechanism, i.e. with the intermediate formation of the corresponding diol with hydroxyl groups in the 1,4-positions. As a result, when the dehydration is run in water vapors the hydrocarbons that are formed have the structure of the catalytic dehydration products of the corresponding glycol – the 2,5-dimethyl-2,5-hexanediol, which should arise in the hydrolytic ring cleavage of the starting 2,2,5,5-tetramethylfuranidine:



And actually, in the catalytic dehydration of 2,5-dimethyl-2,5-hexanediol in the presence of aluminum oxide at the indicated temperature we obtained diisocrotyl in 60% yield; the yield of the fraction, containing the second reaction product – diisobutenyl, was 9%. The total yield of diunsaturated hydrocarbons (69%) proved to be the same as in the dehydration of the corresponding oxide in water vapors (68%), but the ratio between the conjugated and unconjugated dienes that were formed, as was to be expected, changed considerably in favor of the first, as being the compound with the lowest reserve of free energy.

As a result, when conditions exist for the hydrolysis or thionolysis of the 2,2,5,5-tetramethylfuranidine oxide ring in contact with aluminum oxide, then the seeming simple cleavage of water from the cyclic oxide actually occurs as a two-stage reaction, proceeding through the stage of forming the ditertiary 1,4-diol or, correspondingly, the 1,4-mercaptohydroxy compound with subsequent cleavage of two molecules of water or, correspondingly, a molecule of water and a molecule of hydrogen sulfide, which leads to diunsaturated hydrocarbons and, mainly, to the conjugated diene.

If the diol can be formed only partially as the result of the water adsorbed by the aluminum oxide, or evolved in the reaction, then the dehydration of the cyclic oxide, proceeding for the most part without the indicated intermediate stage, leads to a complex mixture of unsaturated hydrocarbons that lend themselves to separation with difficulty.

All of the above is very convincing evidence that the formation of the unsaturated hydrocarbon in the catalytic dehydration of either the alcohol or the 1,4-diol is a one-stage process, for its realization not requiring the intermediate stage of forming the (simple) ether, or, correspondingly, the five-membered cyclic oxide, as is assumed by some authors [4]. The formation of either the (simple) ether or the five-membered cyclic oxide, on the one hand, and of the unsaturated hydrocarbon, on the other, – appear as two independent directions of the catalytic dehydration of the alcohol or, correspondingly, of the 1,4-diol in the presence of aluminum oxide, which take place under different temperature conditions.

EXPERIMENTAL

Catalytic dehydration of 2,2,5,5-tetramethylfuranidine in steam.

32 g 2,2,5,5-tetramethylfuranidine was passed over aluminum oxide at 350° at a rate of 0.5 ml/min., while at the same time from another dropping funnel water was introduced (45 g); the reaction was performed in a weak stream of nitrogen. The catalyzate was collected in a well cooled receiver. The weight of the hydrocarbon catalyzate was 26.6 g. After drying, the obtained mixture of hydrocarbons was distilled at 750 mm in a column with an efficiency of 45 perfect plates and the following fractions were separated: 1) boiling up to 113°, 1.7g; 2) b.p. 113-114°, 5 g; 3) boiling range 115.5-121°, 3.2g; 4) boiling range 121-133°, 0.5 g; 5) b.p. 133-134°, 13.5 g.

Fraction 2 was 2,5-dimethylhexadiene-1,5 (diisobutenyl):

B. p. 113-114° (750 mm), n_D^{20} 1.4290, d_4^{20} 0.7450, MR_D 38.14. $C_8H_{14}\Gamma_2$. Calc. 38.21. Yield 18%.

Literature data: [5] – b.p. 113-114° (755 mm), n_D^{20} 1.4303, d_4^{20} 0.7505; [6] – b.p. 113.1° (741 mm), n_D^{20} 1.4302, d_4^{20} 9.7512.

Fraction 5 was 2,5-dimethylhexadiene-2,4 (diisocrotyl):

B.p. 133-134° (750 mm), n_D^{20} 1.4780, d_4^{20} 0.7630, MR_D 40.58. $C_8H_{14}\overline{F}_2$. Calc. 38.21. EM_D + 2.37. Yield 50%.

Literature data: [5] – b.p. 134-134.5° (747 mm), n_D^{20} 1.4760, d_4^{20} 0.7636; [7] – b.p. 134.3° (750 mm), n_D^{20} 1.4787, d_4^{20} 0.7622.

Catalytic dehydration of 2,5-dimethylhexanediol-2,5.

24 g of 2,5-dimethylhexanediol-2,5 (m.p. 89°) was passed over aluminum oxide (heated to 350°) in a stream of nitrogen. The fused diol was introduced drop-wise into the hot portion of the tube; the catalyzate was collected in a cooled receiver and crystallized therein. The weight of the hydrocarbon layer of the catalyzate was 16 g (90%). Upon distillation of the obtained mixture of hydrocarbons in a column with an efficiency of 45 perfect plates (at 735 mm), the following fractions were separated: 1) boiling range 60-114°, 0.8 g; 2) boiling range 114-121°, 1.6 g; 3) boiling range 121-132°, 1.1 g; 4) b.p. 132-133.2°, 10.5 g.

Fraction 4 was diisocrotyl:

B. p. 132-133.2° (735 mm), n_D^{20} 1.4775, d_4^{20} 0.7634, MR_D 40.84. Yield 60%.

Fraction 2, distilling in range 114-121° (735 mm), n_D^{20} 1.4360, d_4^{20} 0.7462, contained a considerable quantity of diisobutenyl but this hydrocarbon was not isolated in its pure state.

SUMMARY

1. The catalytic dehydration of 2,2,5,5-tetramethylfuranidine in water vapors in the presence of aluminum oxide at 350° proceeds with the predominant formation of diisocrotyl (50% yield) and, together with it, of diisobutenyl (18% yield).

2. The catalytic dehydration of the corresponding diol – 2,5-dimethyl-2,5-hexanediol – in the presence of aluminum oxide at 350° leads to the predominant formation of diisocrotyl (60% yield) and, together with it, of diisobutenyl (9% yield).

3. The mechanism for the dehydration of 2,2,5,5-tetramethylfuranidine in the presence of either hydrogen sulfide or water vapors in contact with aluminum oxide differs from the mechanism for dehydration in the absence of these reagents and includes the intermediate stage of forming the ditertiary 1,4-mercaptohydroxy compound or, correspondingly, the 1,4-diol; the latter, cleaving hydrogen sulfide and water, first give diene hydrocarbons, mainly of the conjugated type.

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REACTION OF A HYDROCHLORIC ACID SOLUTION OF IODINE CHLORIDE WITH BARBITURIC ACID DERIVATIVES

III. THIOBARBITURATES

L. I. Rapaport and Ya. A. Fialkov

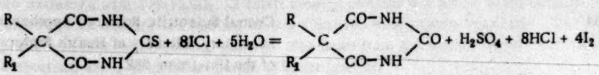
In this communication we describe the results of studying the reaction of ethyl-(methylbutyl)-thiobarbituric acid (thiopental) with iodine chloride in hydrochloric acid medium.

When a hydrochloric acid solution of iodine chloride is added to an aqueous alkaline solution of thiopental at 60-70° there is observed the liberation of iodine and the appearance of sulfate ions in the solution. If this iodine is extracted with chloroform and titrated with $Na_2S_2O_3$ solution, then it is found that the amount of liberated iodine is 4 moles for 1 mole of the thiopental.

It can be assumed that the oxidation of the sulfide sulfur by the iodine chloride in hydrochloric acid medium is accompanied by the formation of HCl and H_2SO_4; consequently, the liquid titrated in the previous experiment was titrated with 0.1 N sodium hydroxide solution (methyl orange indicator).

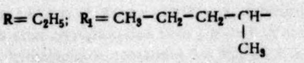
At the same time the amount of 0.1 N NaOH solution required for the titration of the acid in an equal volume of the original hydrochloric acid solution of ICl was determined in the same way. Comparison with the control experiment revealed that the increase in acidity of the investigated solution corresponds to the formation of 10 equivalents of acid for 1 mole of thiopental, where, based on the data obtained for the quantitative determination of sulfate ions, 2 equivalents of the acid belong to H_2SO_4. If the amount of sulfur determined in this way is related back to the thiopental weight, then the amount of found sulfur is very close to the calculated.

The results of these studies gave basis to assume that a hydrochloric acid solution of iodine chloride reacts with thiopental by the following equation:



Thiopental

Ethaminal



$$R = C_2H_5;\ R_1 = CH_3-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

The formation of ethyl-(methylbutyl)-barbituric acid (ethaminal) was confirmed by its isolation from the chloroform solution.

As a result, it must be considered proved that the reaction of thiopental with iodine chloride in hydrochloric acid medium consists in the oxidation of sulfide sulfur, accompanied by the conversion of the thio CS group into the carbonyl group and the formation of 2 equivalents of H_2SO_4, 8 equivalents of HCl and iodine. This reaction is both rapid and quantitative, which permits its use for the quantitative determination of thiopental.

It can be assumed that certain other organic compounds, containing the CS-group, will also react in similar manner with a hydrochloric acid solution of iodine chloride. For example, this is confirmed by the experiments with thiourea, the reaction of which with iodine chloride in hydrochloric acid medium proceeds by the equation:

$$(NH_2)_2CS + 8ICl + 5H_2O = (NH_2)_2CO + H_2SO_4 + 8HCl + 4I_2.$$

EXPERIMENTAL

The thiopental sample (0.15 g) was dissolved in 15 ml of 95% alcohol, and 300 ml of boiling water and 45 ml of a 0.25 N hydrochloric acid solution of iodine chloride was added. After standing for an hour the liquid was boiled. One gram of KI was added to completely destroy the iodine and the mixture was boiled anew to give a colorless solution, after which the amount of sulfate ions was determined gravimetrically as $BaSO_4$.

Found %: S 12.92. $C_{11}H_{18}O_2N_2S$. Calculated %: S 13.23.

The formation of ethyl-(methylbutyl)-barbituric acid in the reaction between thiopental and iodine chloride was shown as follows: after titration of the iodine contained in it the chloroform extract was separated from the water phase, washed with water and made anhydrous with fused sodium sulfate. After evaporating the chloroform the residue was dissolved in 5 ml of 0.1 N NaOH, the solution was filtered, and then acidified with hydrochloric acid; here a crystalline precipitate was obtained, m.p. 125-126°. According to the literature, the melting point of the acid form of ethaminal is 127-130° [1].

The reaction of a 0.1 N iodine chloride solution with a 1% thiourea solution was studied under the same conditions as in the experiments with thiopental. Here we determined the amount of reacted iodine chloride, the total amount of formed hydrochloric and sulfuric acids, and the amount of sulfate ions.

Found %: S 41.33. CH_4N_2S. Calculated %: S 42.13.

SUMMARY

1. The reaction of sulfur-containing barbiturates (thiopental) with a hydrochloric acid solution of iodine chloride proceeds with the oxidation of the sulfur of the CS—group into sulfuric acid and the simultaneous formation of 8 equivalents of hydrochloric acid and 8 equivalents of iodine; here the thiopental is converted into ethyl-(methylbutyl)-barbituric acid.

2. Thiourea reacts with iodine chloride in a similar manner.

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ACONITE ALKALOIDS[*]

VII. MONOACETYLSONGORINE – A NEW ALKALOID FROM ACONITUM SOONGORICUM STAPH.

A. D. Kuzovkov and P. S. Massagetov

Aconitine and songorine were isolated earlier from jungar aconite (Aconitum soongoricum Staph.) by S. Yu. Yunusov [1]. We studied the bases from the mother liquors after these two alkaloids had been removed. After chromatographing on aluminum oxide from chloroform solution under elution of the column with a chloroform-methanol mixture (50:1) we were able to isolate two substances: from the first eluates the base $C_{23}H_{31}O_4N$, previously not found in plants, and songorine from the subsequent fractions. A comparison of the composition of songorine with that of the new alkaloid led to the postulation that the latter is O-monoacetylsongorine. This was confirmed without difficulty when the hydrolysis and acetylation products of the new alkaloid were studied: songorine was obtained in the first instance, and diacetylsongorine in the second.

The infrared spectrum of monoacetylsongorine contains the absorption bands 3448 cm^{-1} (OH-group), 1754 cm^{-1} (ester carbonyl), 1708 cm^{-1} (keto group in a six-membered ring or one of greater number [2]) and 992 and 907 cm^{-1} (CH_2=CH– C – group [3]). The absorption band at 1708 cm^{-1} retains its position in the spectra of both songorine and dihydrosongorine. The 1754 cm^{-1} band disappears when the acetyl group is removed by saponification.

The monoacetylsongorine perchlorate is readily soluble in hot water and difficultly soluble in cold water. After the salt had been obtained, this made it possible to use a simpler method, described in EXPERIMENTAL, for isolating the monoacetylsongorine from the mixture of alkaloids. The dry aconite tubers contain about 0.6% aconitine, 0.06% songorine and 0.01% monoacetylsongorine.

EXPERIMENTAL

Isolation of alkaloids. 90 kg of the dried and pulverized aconite tubers was steeped with 10% aqueous ammonia and exhaustively extracted with benzene. From the benzene solution the alkaloids were extracted with 10% H_2SO_4. A small amount of ether was added to the sulfuric acid extract and upon energetic shaking and cooling, it was alkalized with aqueous ammonia. The crystalline precipitate was filtered off (400 g, part A). The bases from the mother liquor were extracted with ether. We obtained 450 g of an oily mixture of bases (part B).

400 g of the crystalline bases (part A) was dissolved in 1 liter of 15% H_2SO_4 and the solution was cleared with carbon. Upon addition of 300 ml of 30% sodium bromide solution, the aconitine hydrobromide came down which after crystallization from 1.5 liters of water weighed 400 g, melted at 170-171° (the literature for the hydrobromide containing 3.5 H_2O gives m.p. 172-173° [4]). After separation and crystallization of aconitine hydrobromides, the mother solutions were alkalized with ammonia upon which, 120 g of crystalline product separated out (part C).

450 g of the oily mixture of bases (part B) was dissolved in the minimum amount of 20% H_2SO_4. Upon standing, songorine sulfate came down, yield 60 g, m.p. 216-217° (from water). The base, on separation from the sulfate, melted at 201-203°, the hydrobromide at 273-274°, the hydrochloride at 260-261°, and the nitrate at 255-256°; these constants corresponded to those given in the literature [1].

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[*] Cf. J. Gen. Chem. 25, 2345 (1955) for the previous communications; (p. 2317, C. B. Translation).

120 g of crystalline bases (part C) was dissolved in 10% H_2SO_4; the solution was combined with the mother solutions remaining on separation of songorine sulfate. Upon addition of sodium bromide solution, aconitine hydrobromide came down which after crystallization from water weighed 150 g. After separation and crystallization of this hydrobromide, a solution of magnesium perchlorate was added to the mother liquors until precipitation was complete. The solution was decanted from the oily precipitate which came down; on boiling the latter with water it crystallized. 50 g of aconitine perchlorate was filtered off from the hot solution. From the mother liquors (from the precipitation of the perchlorate and from the treatment of the precipitate with boiling water) after addition of ammonium chloride and alkalization with aqueous ammonia, we extracted (with ether) 200 g of oily bases (part D) which was separated into 10 fractions. For this, a solution of bases in 5% H_2SO_4 was fractionally alkalized with 10 equal portions of NaOH solution with ether extraction after each addition of alkali. From the least basic fractions (2-4) we obtained 16 g of impure perchlorate monoacetylsongorine, which after crystallization from 50% methanol, melted at 242-243°. From the more basic fractions (6-10), upon solution in 10% HCl, we isolated 29 g of songorine hydrochloride.

Monoacetylsongorine. Monoacetylsongorine was isolated in the usual manner from the perchlorate, m.p. 242-243° and after crystallization from alcohol or acetone, it melted at 176.4-178.5° (the base, isolated from the recrystallized hydrochloride also melted at the same temperature).

44.0 mg substance in 10 ml of CH_3OH, l 1dm, α -0.89°, $[\alpha]_D$ -202.5°.

Found %: C 71.55, 71.77; H 8.02, 7.96; N 3.54, 3.34. $C_{23}H_{31}O_4N$. Calculated %: C 71.67; H 8.11; N 3.64.

Monoacetylsongorine hydrochloride was prepared from the base in alcoholic solution, m.p. 285-286° (from aqueous alcohol).

0.6530 g of substance in 10 ml of H_2O, l 1 dm, α -11.22°, $[\alpha]_D$ -171.9°.

Monoacetylsongorine perchlorate was prepared from the hydrochloride in aqueous solution, m.p. 272-273° (from 50% methanol).

Acetylation of monoacetylsongorine. 0.6 g of monoacetylsongorine was boiled with an excess of acetyl chloride for 1 hour. After crystallization from ether, the reaction product melted at 180-181° (in vacuum 194-194.5°), a test mixture with diacetylsongorine [1] melted at the same temperature. The hydrochloride of the acetylation product, obtained in aqueous solution, melted at about 180° and then solidified and melted again at 243-244° (with decomposition). Diacetylsongorine hydrochloride [1] and its test mixture with the product also melted at the same temperature.

SUMMARY

A new alkaloid was isolated from the jungar aconite (Aconitum soongoricum Staph.), being the previously unknown monoacetylsongorine.

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ALKALOIDS OF LEONTICE EWERSMANNII BGE

III.* LEONTINE, THE STRUCTURE OF THE HETEROCYCLIC NUCLEUS

T. F. Platonova and A. D. Kuzovkov

Leontine $C_{15}H_{24}ON_2$ was first isolated from the plant Leontice Ewersmannii by A. P. Orekhov and R. I. Konovalova [2] as the picrate; then it was characterized in detail by S. Yu. Yunusov and L. G. Sorokina [3], who were also responsible for its name. Later we isolated an alkaloid from Leontice Ewersmannii, the constants of which all coincided with those of leontine, the only exception to this agreement being the specific rotation. Leontine was described by S. Yu. Yunusov and L. G. Sorokina as being optically inactive; we obtained a levorotatory base with $c[\alpha]_D - 78.2°$ (c = 14.4, anhydrous alcohol). This alkaloid was named isoleontine. After our paper had been published we proceeded to isolate and séparate the alkaloids from different Leontice Ewersmannii specimens. In all cases we obtained isoleontine with the earlier determined specific rotation value; leontine was not found. It could be assumed that S. Yu. Yunusov and L. G. Sorokina made an error in determining the specific rotation, and that leontine and isoleontine represent the same substance. Leaving the name of leontine for the alkaloid, it must be assumed that its specific rotation is equal to the value given above.

In our published paper it was established that leontine belongs to the matrine group of alkaloids, which ensues from a comparison of the reduction products of leontine and matrine.

It is known that when the carbonyl group in matrine is reduced, either by distillation with zinc dust or in the presence of a catalyst ($CuCrO_4$) at a pressure of 120 atm. [4], that a substance named matridine is formed. (±)-Matridine was synthesized by Schopf and coworkers [5], and was cleaved by them into the (+)- and (−)-isomers, of which the first is identical with matridine.

In the catalytic reduction of the carbonyl group in leontine with the Pt from PtO_2 in hydrochloric acid we obtained earlier an oxygen-free substance, namely isoleontane, also formed in the reduction of leontine with $LiAlH_4$. The ability of the CO-group to be reduced under these conditions to the methylene group indicates its lactam character.

The constants given in the literature for (−)-matridine lie close to the constants of isoleontane. For purposes of direct comparison we had the possibility of obtaining (+)-matridine, which was realized by the hydrogenation of matrine with the Pt from PtO_2 in hydrochloric acid solution. The constants of the substance synthesized in this manner coincide with those of isoleontane, with the exception of the specific rotation sign (cf. table). When mixed with isoleontane a racemate was formed, which melted at the same temperature as (+)-matridine. The infrared absorption spectra of isoleontane and (+)-matridine coincide completely. The presented data demonstrate the identity of isoleontane with (−)-matridine. In this way the structure of a heterocyclic nucleus is determined for leontine. Although both leontine and matrine have the same composition, still they differ in all of their physical constants, for which reason they cannot be anitpodes and should differ in the position of the carbonyl group. Four positions are possible for the lactam carbonyl in the matridine nucleus. One of the formulas expresses the structure of matrine (I); the structure of leontine should be expressed by one of the other three formulas: (II), (III) or (IV).

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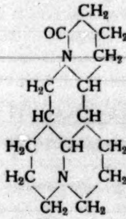
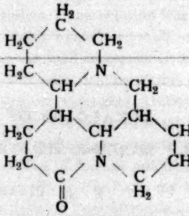
* Cf. [1] for Communications I and II.



(I)



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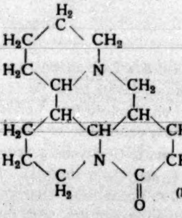

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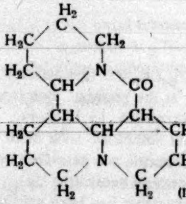

(IV)

TABLE

Constants of Isoleontane and (+)-Matridine

Alkaloid	Base *		Hydrochloride		Methiodide		Picrate
	Melting point	$[\alpha]_D$	Melting point	$[\alpha]_D$	Melting point	$[\alpha]_D$	Melting point
Isoleontane	77-79°	−30.1°	368°	−14.7°	292°	−5.3°	256°
(+)-Matridine	76-77.5	+29.7	368	+12.4	293	+5.4	258
	(76-77)	(−28.2)					

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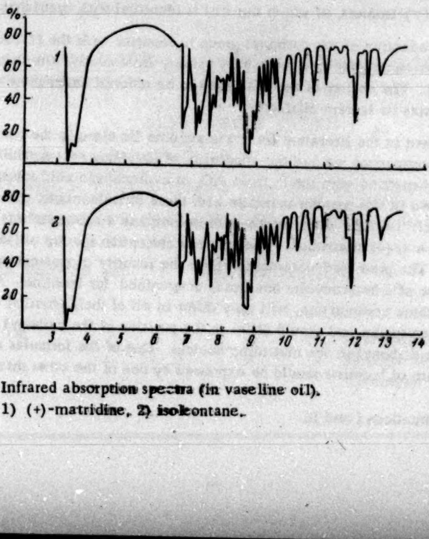
* The constants given in the literature for (−)-matridine are shown in parentheses [5].



Infrared absorption spectra (in vaseline oil).
1) (+)-matridine, 2) isoleontane.

EXPERIMENTAL

1. Reduction of leontine with $LiAlH_4$. Preparation of isoleontane. 2 g leontine in 500 ml of absolute ether was reduced with 0.8 g of $LiAlH_4$ (boiled for 5 hours), the solution was evaporated down to 100 ml and 2-3 ml of water was carefully added to the residue. The ethereal layer was separated off. The aqueous layer was extracted with ether. From the combined ethereal extracts we isolated 1.9 g of isoleontane; m.p. 77-79° (from ether).

2. Hydrogenation of matrine. Preparation of (+)-matridine. 2 g of matrine in 100 ml of 1 N HCl was hydrogenated, using Pt obtained from 1 g of PtO_2, at 70-90° in the course of 24 hours. About 260 ml of H_2 was absorbed. After separation of the catalyst, the solution was evaporated down in vacuum to low bulk, alkalized with 40% NaOH and extracted with ether. We isolated 1.2 g of the crude base. After vacuum-distillation (boiling range 155-160° at 10 mm), the compound crystallized (0.9 g). The hydrochloride was prepared by mixing together the alcoholic solutions of the base and hydrogen chloride; it melted at 368° (from alcohol), $[\alpha]_D$ +12.4° (c = 4.9, alcohol). Upon isolation of the base from the hydrochloride, it melted at 76-77.5° (from ether), $[\alpha]_D$ = 29.7° (c = 4.1, anhydrous alcohol).

Found %: C 76.99, 76.93; H 10.98, 11.05; N 11.56, 11.60. $C_{15}H_{26}N_2$. Calculated %: C 76.85; H 11.19; N 11.95.

Methyl iodide was added to a solution of the base in acetone. Upon standing, the methiodide came down; decomposed at 293° (from 70% alcohol), $[\alpha]_D$ +5.4° (c = 4.1, water).

The picrate was prepared by mixing alcoholic solutions of the base and picric acid. It melted at 258° (from a acetone-alcohol mixture).

3. Preparation of the racemate. A mixture of 0.1200 g of (+)-matridine and 0.1200 g of isoleontane was recrystallized from ether; we isolated the racemate, m.p. 55-56°. [In the literature it is described as (±)-matridine, m.p. 55°] [5]. When it was mixed with isoleontane and (+)-matridine, a melting point depression was observed. From the racemic base we prepared the hydrochloride, m.p. 340° (from alcohol), $[\alpha]_D$ 0° ± 0.01° (c = 11.1, water).

SUMMARY

1. It was established that the (−)-matridine nucleus lies at the base of leontine.

2. Leontine belongs to the matrine group of alkaloids.

3. Leontine differs from matrine in the position of the lactam carbonyl and in the configuration of the asymmetric centers. Three possible formulas for leontine were proposed.

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